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A CHEMICAL STUDY OF RANCIDITY III. SOME RECENT DEVELOPMENTS IN THE STUDY OF OXIDATIVE RANCIDITY OF SPECIAL INTEREST TO THE CEREAL INDUSTRY 1

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An increasing interest is being evidenced by various branches of the food industry in the spoilage of foods through rancidity development. The first industries to be concerned were the manufacturers of butter and edible shortenings due to the necessity of producing a product that could be stored and marketed without appreciable deterioration. The bakers of certain goods, particularly crackers, also became interested because of the possibilities of rancidity development in their product. The advent, during the past few years, of prepared and packaged biscuit flours and doughs containing large amounts of shortening agents has also necessitated a serious consideration of rancidity problems. From a nutritional standpoint it has been demonstrated that rancid fats exert a destructive effect on certain of the vitamins. These facts emphasize the widespread occurrence of rancidity problems in the food industry and the reason for considering some advances made in this study during the past few years.

Terminology

One encouraging advance of the past few years in regard to a clearer understanding of rancidity problems has been the more careful use of the term rancidity. In the past, this term has been used rather loosely to include any or all of the three types of fat spoilage, which have been classified by Triebold (1931) as oxidative, hydrolytic, and ketonic rancidity.

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At present, a group of investigators, considering only one particular fat, are using the term rancidity in a very restricted sense to include only that spoilage where butyric acid is liberated. The majority of investigators, however, dealing with the numerous fats and oils of industry are using the term to include all the types of rancidity, but with enough description to clearly designate the type involved. This more careful use of the term has eliminated much of the past confusion regarding the causes, effects, and methods of preventing rancidity. Since oxidative rancidity is the type usually encountered in the cereal industry, it is the only type considered in this paper.

Susceptibility of Fats to Oxidative Rancidity

Considerable variations in susceptibility to oxidative rancidity are experienced between individual samples of the same type of fat as well as between different types. Various reasons have been suggested to account for this difference in behavior of the fats, and, it is likely, that all the reasons advanced play a part in the final explanation of this phenomenon.

Differences in Susceptibility to Oxidative Rancidity between Types of Fats

Without a doubt, the difference in susceptibility to oxidative rancidity between the various types of fats is influenced, in a large measure, by the character of their fatty acids combined as glycerides. It is obvious, that if oxidative deterioration involves particularly the unsaturated acids, as all theories postulate, then those fats containing the lesser amount of unsaturated glycerides, and, more especially, the lesser amount of highly unsaturated ones such as linolic and linolenic acid glycerides, will have the least susceptibility to oxidative rancidity. The excellent keeping qualities of cocoanut oil, consisting principally of saturated acid glycerides, appears to confirm this idea. So also does the improved keeping qualities of cottonseed oil after selective hydrogenation of the highly unsaturated glycerides.

Another interesting example of the influence of structure on the ease of oxidation is illustrated in the work of Täufel and Spiegelberg (1930). They have shown that in the case of the cis-trans isomers, oleic and elaidic acids,

$$\begin{array}{cccc} \mathrm{CH_3^-(CH_2)_7^-CH} & \mathrm{CH_3(CH_2)_7CH} \\ \parallel & & \parallel \\ \mathrm{HOOC(CH_2)_7CH} & \mathrm{HC-(CH_2)_7COOH} \\ \mathrm{(cis-form)} & \mathrm{(trans-form)} \end{array}$$

that the oleic acid reacts much more readily with oxygen than its isomer, elaidic acid. The difference in reactivity between these two acids has

suggested to us another reason for the greater resistance to oxidation of hydrogenated shortenings. It had been pointed out by Hilditch (1927) that

"Since the ethylenic linkages in a highly unsaturated fatty acid occur at different points in the chain of carbon atoms, it is easy to understand why the oleic acids produced by selective hydrogenation are not all the same and identical with the ordinary oleic acid $\Delta^{9:10}$ —octadecanoic acid—the double bond left unsaturated may well be one of the others."

In our opinion, this effect of hydrogenation results in the formation of isomeric oleic acid glycerides differing from the naturally occurring oleic acid glycerides not only in physical properties but also in reactivity towards oxygen.

Differences in Susceptibility to Oxidative Rancidity between Individual Fats of the Same Type

Individual fat samples within a type exhibit considerable variations with respect to susceptibility to oxidative rancidity. This can be accounted for on the basis that fats vary in their content of pro-oxygenic catalysts due to their past treatment and to contamination with foreign materials. Such conditions of past treatment which favor the formation of peroxide or moloxide compounds (high oxidizing potential) will increase susceptibility to autoxidation according to the amount of these peroxide compounds formed. Contamination of the fat with certain metals tremendously influences the susceptibility to autoxidation. Davies (1932) lists the following metals in the order of their effect as pro-oxygenic catalysts: (1) Vanadium, (2) copper, and (3) iron, nickel, and manganese.

Triebold (1929) suggested that differences in susceptibility of individual fats to autoxidation, as measured by the length of induction period, might be accounted for by varying amounts of anti-oxygenic substances contained in the fats. A similar idea has been suggested recently by Hilditch and Sleightholme (1932), who have demonstrated by experiments on four oil samples, that the original oils were more resistant to autoxidation than either the saponified oil, re-esterified fatty acids of the oils, or glycerides prepared synthetically from the distilled acids of the oils. It is very likely that the susceptibility to autoxidation of many of the fats and oils, particularly those which do not undergo a drastic refining process, is influenced to a considerable degree by the presence of anti-oxygenic substances.

Methods of Determining the Susceptibility of Fats to Oxidative Rancidity

Several investigators (Holm and Greenbank, 1923; Greenbank and Holm, 1925, 1930; Hilditch and Sleightholme, 1932; Mattill, 1931;

Triebold and Bailey, 1932) have used controlled oxidation studies to determine the effect of various factors in the oxidative deterioration of fats. Although all these methods are the same in principle, they vary considerably in detail. For example, variations in the temperature of autoxidation may range from room temperature to 95° C., stirring is employed in some methods and not in others, while one method uses light as a catalyst instead of heat.

We have made a comparison of the results obtained by controlled autoxidation of lards at 95°, 90°, 70° C. without stirring, and 95° C. with stirring, using the Holm and Greenbank (1923) gas-tight stirrer, and have found, in general, that all the methods rank the samples in approximately the same relative order with respect to keeping ability. Stirring does not appear to influence the results as evidently there is no appreciable surface film formation through polymerization, although this would likely be a factor in the case of the drying oils. Since this study was made, we have adopted, when stirring is necessary, the mercury seal stirrer as used by Briggs (1931) thereby eliminating the inherent difficulties of the Holm and Greenbank stirrer, namely, the danger of contamination with metallic catalysts, and of not obtaining an absolutely gas-tight seal in the bearing. There is a possibility that if the fat contains metal catalysts, temperatures over 75° C. may lead to erroneous results. Ellis (1932) has demonstrated that using cobaltous oleate as a catalyst, he could effect a considerable autoxidation of even the saturated fatty acids such as stearic acid at temperatures over 75° C. However, in the absence of catalyst, he got no oxidation of the saturated acids at the higher temperatures. We have found in the case of pure myristic acid, that even after 25 hours exposure to oxygen at 90° C. it had not begun to autoxidize. These results would tend to indicate that ordinarily the choice of a controlled oxidation method would limit itself to the ease and speed of obtaining results.

Method of Determining the Susceptibility of Crackers to Oxidative Rancidity

It is now generally accepted that the length of induction period of a fat, as determined by any of the controlled oxidation methods, is a good index of the susceptibility of that fat to oxidative rancidity. It was thought likely that a comparable relationship would hold between the length of induction period of a fat and the susceptibility to oxidative rancidity of crackers in which the fat was used as a shortening agent. While, in general, it was found by Triebold and Bailey (1932) that such a relationship seemed to exist, several outstanding exceptions were noted where the keeping quality of a fat baked into crackers was greatly enhanced over that indicated by the length of induction period of the

fat itself. However, the length of induction period determined on the crackers themselves was found to be a much better criterion for judging the susceptibility of crackers to oxidative rancidity.

Since the results of Triebold and Bailey (1932) were obtained on commercial crackers produced under very dissimilar conditions it was thought advisable to conduct a similar type of study on experimental crackers baked under standard conditions and thereby eliminating all variables except the shortening agent. Ten samples of lard shortenings were secured and baked into experimental crackers, attempting as much as possible to duplicate the formulas and procedures used in the baking of commercial crackers.

All the lards were autoxidized at 95° C. without stirring in an apparatus similar to that described by Triebold and Bailey (1932) to determine the lengths of their induction periods. Free acidities were determined according to the official method (A. O. A. C. Book of Methods, 1931, p. 326). The original method of Blunt and Feeney (1915) was used to obtain the smoking temperatures since the method as modified by McCoy (1931) did not yield better results. The peroxide contents as measured by the active oxygen values were determined by the method of Lea (1931) and reported as the cubic centimeters of N/500 sodium thiosulphate solution required to react with the iodine liberated from potassium iodide by 1 gm. of fat. Schibsted's (1932) method was used to ascertain the amount of aldehydes present in the fat and calculated according to his formula as the fat-aldehyde value. To obtain a measure of the keeping qualities of the lards, samples were stored at room temperature and at 40° C. and the number of days determined until the samples possessed the characteristics of oxidative rancidity, i.e., gave a definitely positive Kreis test and the characteristic rancid odor.

Keeping quality of the experimental crackers was ascertained by storage tests at 40° C. and noting the number of days required before they developed a rancid odor. Lengths of induction periods were also determined on the crackers by autoxidation at 95° C.

The results of this study are summarized in Table I, together with all the definite coefficients of rank of correlation obtained between the factors considered. The coefficient of rank of correlation (Jackson, 1924) was preferred to the straight coefficient of correlation since it was not desired in this case to correlate absolute values but rather to determine ability to rank one factor in respect to another. It is appreciated that the number of samples used in this study was so small that any conclusions drawn are simply indicative of what may be expected to occur.

Triebold and Bailey (1932) found a close relationship between the length of induction period of commercial crackers and their keeping

qualities and this same relationship holds for the experimental crackers reported in Table I. The coefficient of rank of correlation found $+.927\pm.031$, exemplifies the ability with which it is possible to rank the crackers in order of their keeping qualities and emphasizes the fact that the determination of the length of induction period on crackers provides us with a rapid and yet accurate method for evaluating the keeping qualities of such baked goods.

TABLE I

A Comparison of the Keeping Quality of Experimental Crackers with Various Characteristics of the Lard Shortenings Used in Their Production

All definite coefficients of rank of correlation obtained between the various factors are indicated.

Canalaga			Lards						
Sample number	Days sweet (Storage at 40° C.)	Induc- tion period in hours		Days sweet (Stor- age	Induc- tion period in hours	Free acidity Mgs. of KOH per gram of fat	Smok- ing tempera- ture	Na ₂ S ₂ O ₃	aldehyde
10	31 +	5.25	0	0	0.66	0.886	197.5	9.20	2.70
10 7 9 8 1	31	4.50	0	0	0.50	0.836	185.0	2.80	1.80
9	30	3.87	50	30	4.25	0.875	200.0	1.50	0.25
8	29	3.45	11	_	1.00	0.842	191.0	2.30	0.50
1	25	4.00	63	32	1.25	0.673	187.0	4.55	2.00
3	24	3.25	78	30	5.16	0.954	198.0	1.60	0.25
6	20	3.20	-	15	3.75	0.757	224.0	1.52	0.28
2	20	3.08	66	25	2.75	1.038	187.0	2.50	0.44
3 6 2 4 5	20	2.50	26	15	2.00	0.870	197.0	2.30	1.30
5	13	2.70	24	10	1.08	2.637	163.0	1.65	0.10

COEFFICIENTS OF RANK OF CORRELATION

Between induction period of crackers and the days they re-	
mained sweet at 40° C.	$r = +.927 \pm .031$
mained sweet at 40° C. Between lard remaining sweet at room temperature and at 40° C.	$r = +.851 \pm .069$
Between induction period of lards and the days sweet at room	
temperature.	$r = +.896 \pm .046$
Between induction period of lards and their active oxygen con-	
tent.	$r =806 \pm .078$
Between fat aldehyde value of lards and their active oxygen	
content.	$r = +.867 \pm .055$

As would be expected, there was a fairly close relationship between the keeping qualities of the lard samples at room temperature and at 40° C. This substantiates the practice of using a comparatively simple incubation test at an elevated temperature as described by Schaal (1931) for the rapid determination of the keeping quality of fats. A close relationship was also evidenced between the keeping quality of the lards at room temperature and the length of their induction periods which is in accordance with the generally accepted idea that the length of induction period of a fat is a good index of its keeping quality.

No definite correlation was found between the free acidities of the lards and their keeping qualities on storage or their lengths of induction periods. The acidity values for all the samples were very similar except one lard, which had a value three times as large as the rest, and which also evidenced poor keeping quality. These results are also in agreement with those reported by Triebold and Bailey (1932a) in which it was found that only exceptionally high or low acidities were correlated with the keeping qualities of a fat.

While no significant correlation was reported between the length of induction period of the lards and their smoking temperatures, a slight correlation was evident. A much closer relationship was exhibited, however, between the length of induction period and active oxygen values of the lards. It would be expected that the active oxygen (or peroxide) values, since they give an indication of the oxidizing potential already built up in the samples, would be closely related to the lengths of induction periods of the lards. Only two high active oxygen values were obtained among the samples (Nos. 10 and 1) and these both had short induction periods. A good correlation was also experienced between the active oxygen and fat-aldehyde values. This would seem to indicate that in the early stages of oxidation, at least, the formation of aldehydes proceeds at a rate related in some measure to that of the peroxides. In these early stages of oxidation it should be possible then to test equally well for oxidative rancidity by means of either peroxide or aldehyde tests. As the oxidation progresses it is questionable if this relationship continues since Schibsted (1932) reports several cases of strongly oxidized fats with very low fat-aldehyde values.

It is significant to note the absence of a definite correlation between the lengths of induction periods of the lards and the keeping qualities of the crackers produced from them. An examination of the data on individual samples recorded in Table I shows why such a relationship did not exist in this study. The two cracker samples exhibiting the best keeping qualities (Nos. 10 and 7) were produced from lards with the shortest induction periods. Two other cracker samples (Nos. 8 and 1), possessing very good keeping qualities, were also made from lards possessing relatively short induction periods. This study would seem to indicate that shortenings of poor keeping quality may be used to produce crackers of good keeping quality, and this emphasizes a very important fact—that one cannot justly evaluate a shortening for its use in cracker manufacture by simply making a study on the shortening itself.

Inferior Shortenings Produce Crackers of Superior Keeping Quality

Triebold and Bailey (1932) found in the case of commercial crackers that a relationship seemed to exist between the length of induction period of a fat and its keeping quality when baked into crackers. However, several outstanding examples were also reported by them where lards of exceptionally poor keeping quality were used to produce crackers possessing good keeping quality. A possible explanation offered for this behavior was that the wheat oil present in the cracker flour might influence the keeping quality of the crackers. Wheat oil could not be responsible, however, in the case of the experimental crackers since they were all made from the same flour. Thus some reasonable explanation was desired to account for the excellent keeping qualities possessed by some crackers made from shortenings of inferior keeping qualities.

A possible hypothesis was suggested to account for this behavior. It would seem logical to assume that in the case of certain shortenings which had received good treatment and had undergone no appreciable deterioration before being baked into crackers, that a relationship would likely exist between the lengths of their induction periods and the keeping quality of the crackers in which they were used. On the same basis, if such shortenings were old or mistreated so that they had undergone incipient oxidation, this should be reflected in the lengths of induction periods and keeping qualities of the shortenings. It should be conceivable, however, that such shortenings when baked into crackers might have these deteriorative effects destroyed in the baking process and the resulting crackers should then possess keeping qualities comparable to those expected from the fresh shortening. Thus it might be possible to account for the ability of an inferior shortening in the incipient stages of oxidative rancidity to be used in the production of crackers with superior keeping qualities.

A short study was outlined to test the validity of this hypothesis. Two lard samples, one an open kettle and the other a prime steam rendered, were autoxidized to definite oxygen absorptions. After determining the lengths of induction periods and active oxygen (or peroxide) values on the two control and six oxidized samples, they were baked into experimental crackers. Within a week after baking, the lengths of induction periods were determined on the crackers, and active oxygen values obtained on the fat extracted from the crackers with petroleum ether. A small fraction of each of the cracker samples was stored at room temperature but up to the present none of these samples have shown any signs of oxidative rancidity.

The results of this study, summarized in Table II, appear to confirm the validity of the hypothesis presented. It is clearly indicated that autoxidation of a lard to a limited degree increases the active oxygen content considerably and decreases or entirely eliminates the induction period. Crackers produced from the lards with high active oxygen values show materially reduced active oxygen contents for their extracted fat. The lengths of induction periods of the cracker samples have been increased in all cases over the lengths of induction periods of the corresponding lard samples and bear no relationship to either the lengths of induction periods or active oxygen values of the lards.

TABLE II

A Comparison of the Length of Induction Period of Experimental Crackers Containing Lard Shortenings Oxidized to Different Degrees with the Length of Induction Period of the Lards and, Also, the Active Oxygen Values of the Lards and the Extracted Fat from the Crackers

Length of induction periods determined by the static method at 90° C.

	Lard sh	ortenings	Cra	ckers
	Induction period in hours	Active oxygen content (cc. N/500 Na ₂ S ₂ O ₃ per gram of fat)	Induction period in hours	Active oxygen content (cc. N/500 Na ₂ S ₂ O ₃ per gram of fat)
Open kettle rendered lard	2.0	1.0		1.7
Control Open kettle rendered lard	3.0	1.6	8.0	1.7
Oxidized to beginning of the				
induction period	0.75	3.6	8.0	5.8
Open kettle rendered lard Oxidized to 15 cc. O ₂ absorption				
per 100 gms. lard	0.0	14.7	8.0	5.0
Open kettle rendered lard				
Oxidized to 50 cc. O ₂ absorption	0.0	39.5	8.0	3.2
per 100 gms. lard Prime steam rendered lard	0.0	39.3	8.0	3.2
Control	1.75	3.8	9.5	4.4
Prime steam rendered lard				
Oxidized to beginning of the	0.0	13.9	9.5	3.2
induction period Prime steam rendered lard	0.0	13.9	9.5	3.2
Oxidized to 15 cc. O ₂ absorption				
per 100 gms. lard	0.0	21.9	5.0	3.7
Prime steam rendered lard				
Oxidized to 50 cc. O ₂ absorption per 100 gms. lard	0.0	41.5	5.0	9.3

The relatively long and similar induction periods of crackers produced from the open kettle rendered lards in the various stages of autoxidation are to be expected as due to the reduction of the active oxygen contents of the lards in the baking process, and thereby, the removal of pro-oxygenic catalysts formed in the preliminary autoxidation of the lard. This same relationship holds in the prime steam lard samples with the exception of one case (crackers produced from the

lard sample autoxidized to 15 cc. of oxygen per 100 gms. of lard), which had a shorter induction period than the other cracker samples of the same active oxygen content. No explanation can be offered to account for this result. The shorter induction period of the crackers produced from the most highly autoxidized prime steam lard is due, in all probability, to the higher active oxygen content of the crackers. A comparison of the active oxygen values for the two types of lards and their behavior when baked into crackers would seem to indicate that autoxidation, in the case of the prime steam lards proceeds to a greater degree per unit of oxygen absorbed than is true of the open kettle rendered lards.

While this preliminary study would seem to indicate that it may be possible for a baker to use a lard shortening which is in the incipient stages of oxidative rancidity and yet produce crackers of good keeping quality, this is certainly not to be recommended as a general practice. A more detailed study must necessarily be made of the whole problem. The important fact derived from this study is that the keeping quality of a shortening as measured by storage tests or length of induction period of oxygen absorption may not be a true index of the keeping quality of the crackers baked from it.

Anti-oxygens

One phase of the rancidity problem which is receiving a great deal of attention at the present time is the study of anti-oxygenic catalysts. This study has followed three main lines of investigation: (1) A search for new anti-oxygens, (2) fundamental studies to account for the action of anti-oxygens, and (3) an attempt to determine the nature of anti-oxygens naturally present in fats.

A survey of the literature reveals numerous experiments to determine the applicability of substances as anti-oxygens for fats. Many of these substances which show such action have been patented and are finding commercial application in the preservation of fats for other than edible purposes. These anti-oxygenic substances vary considerably in structure although most of them used are aromatic amines or phenolic compounds. A partial list of these anti-oxygenic substances for fats which have been studied or patented the past few years would include the following: pyrogallol, pyrocatechol, α -naphthol, β -naphthol, β -naphthoquinone, hydroquinone, quinone, guaiacol, resorcinol, orcinol, phloroglucinol, thymol, o-cresol, p-cresol, eugenol, gossypol, α -naphthylamine, diphenylhydrazine, diphenylamine, diphenylguanidine, phenyl- α -naphthylamine, o-nitroaniline.

Due to the involved nature of the subject it would be impossible in a paper of this length to attempt to discuss the fundamental work relative to the theories of anti-oxygenic action and anyone desiring such information is referred to the original articles. A discussion of the early theories on anti-oxygens will be found in a paper by Moureau and Dufraisse (1926); later modifications are found in papers by Bäckstrom (1927), Mattill (1931), and Milas (1932).

Attempts to ascertain the nature of the substances responsible for anti-oxygenic activity in natural fats and oils dates from the work of Mattill (1927) in which he showed that wheat oil contained something which prevented the oxidation of vitamins A and E. This anti-oxygenic activity was considered by Mattill due to sterols present in the oil and this idea appeared to be substantiated later by the experiments of Mattill and Crawford (1930) in which it was demonstrated that sterols from corn oil prolonged the induction period of a lard-cod-liver oil mixture. Just which vegetable sterols are responsible for this action has not been determined due to the difficulty of their separation. Mattill (1931) found sitosterol, prepared from three different plant sources, without effect, as was also ergosterol and cholesterol.

Not all wheat oils necessarily possess anti-oxygenic activity according to Roller (1931), who found that some were totally inactive in this respect. He found the acetyl values of the active oils to be approximately 30 as compared to 15 for the inactive oils, and also concluded that the anti-oxygenic activity was connected with the "OH group.

Olcott and Mattill (1931) isolated and crystallized an anti-oxygenic material from lettuce which analyzed for a molecular weight of 250, and a possible formula of C₁₃H₁₄O₅. It was only slightly soluble in water and petroleum ether but soluble in ether, acetone, and dilute alkali. It would not add bromine, nor give a Libermann-Burchard test although an acetyl derivative could be formed. Using the autoxidation method of Mattill (1931) the substance had an anti-oxygenic index of 29 as compared to 31 for a-naphthol, indicating that it was a potent anti-oxygen.

Hilditch and Sleightholme (1932) have attacked the problem from a somewhat different angle. These investigators have attempted to determine the effect of the treatment of fats with certain reagents on the length of the induction period. They found, for example, that treatment with aqueous HCl or alkali almost eliminated the induction period in an olive oil sample and concluded from this that the natural anti-oxygenic substances present in this oil are water-soluble products readily removed by comparatively mild reagents. Treatment of the olive oil with sulphuric acid increased its resistance to oxidation indicating the possibility that the sulphuric acid is added at the double bond. While Hilditch and Sleightholme offer no suggestion as to the nature of the anti-oxygenic substances naturally present in fats and oils, they

make the pertinent statement that it is not likely that such anti-oxygens belong in all cases to the same class of substances.

A recent notice to the effect that Greenbank had discovered and patented a new anti-oxygen capable of being used in edible fats was recently reported in Science (News Supplement, Vol. 77, No. 1991, p. 6, 1933). In attempting to determine the anti-oxygenic substances naturally present in fats, Greenbank isolated extremely small amounts of unidentified organic acids. He then tried adding organic acids of known composition to oil and found that maleic acid added in the proportion of 1 part in 10,000 of oil would lengthen the keeping ability from 3–5 times. The mechanism of the reaction is unknown but the suggestion is made that it perhaps operates by stopping the formation of peroxides.

The structure of maleic acid [CO₂H.CH:CH.CO₂H] differs considerably from the previously noted anti-oxygens used in fats which were mostly organic amines or phenolic compounds. Since it is such a relatively simple compound as compared with the ordinary anti-oxygens, it should make an excellent substance for the study of the mechanism of anti-oxygenic action.

The report in Science on maleic acid unfortunately gives no details as to the method used for ascertaining the keeping ability of the oils treated with the anti-oxygen. We have determined the effect of maleic acid on the length of induction period of a few samples of open kettle and prime steam rendered lard and have found that maleic acid in concentration of 0.02% and 0.2% did not appreciably lengthen the induction periods of the lards studied when autoxidized at 90° without stirring. It is possible that in the case of some oils with longer induction periods, that the effect of maleic acid would become more pronounced since the report in Science indicates that Greenbank found "the better the quality of the oil the longer it would be preserved." It is also possible, of course, that the length of induction period as determined at 90° C. does not give a true picture of the anti-oxygenic effect of maleic acid and that storage tests at room temperature are necessary.

Lecithin has been suggested at various times as a possible antioxygenic substance in fats. Roller (1931), however, found that lecithin did not lengthen the induction period of oils or foods containing oils. We have obtained results similar to those of Roller on lecithin and also with choline derived from lecithin.

At the present we must consider that the exact nature of these anti-oxygenic substances is still unknown. The isolation by Bruson, Sebrell and Vogt (1927) of three natural oxidation inhibitors in rubber, two of which were sterols ($C_{27}H_{42}O_3$ and $C_{20}H_{30}O$) and one a phenolic compound illustrates the types of anti-oxygens possible in a plant material

such as rubber. The work of Mattill (1927), Mattill and Crawford (1930), Olcott and Mattill (1931) and Roller (1931) suggests the possibilities of sterol and phenolic compounds as anti-oxygens associated with the plant oils. Hilditch and Sleightholme (1932) found that the natural anti-oxygens present in the oils they examined were watersoluble substances. Greenbank appears to consider traces of organic acids as possible natural anti-oxygens and suggests maleic acid as such a substance. These results indicate that the natural anti-oxygens may belong to several types of substances and that they are likely sterols, phenols or organic acids.

The identification of the natural anti-oxygens present in fats and oils is a very important problem due to its commercial possibilities. A knowledge of the nature of these substances would be of great value for the intelligent preservation of these natural inhibitors during the processing of fats and oils for market. There would also be the possibility of adding natural substances to fats and foods without questionable physiological effects on the consumer or the prejudice against the addition of such things as chemical preservatives to natural food

materials.

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SPECTROPHOTOMETRIC DETERMINATION OF THE CAROTINOID PIGMENT CONTENT OF WHEAT FLOUR

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Since a method for the quantitative determination of the carotinoid pigments in flour by a spectrophotometric procedure was published by Ferrari and Bailey (1929, 1929a) the method has been improved in several particulars. It is purposed to describe here the procedure and instrumental set-up used at the present time in this laboratory. This description will be presented in three parts, viz.: I. Description of spectrophotometric equipment; II. Preparation of the flour extract; III. Spectrophotometric procedure for the quantitative determination of the carotinoid pigments of wheat flour.

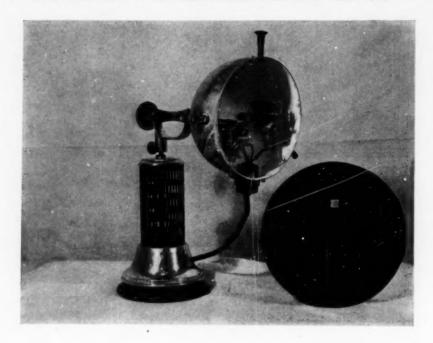
In carrying out a large number of determinations convenience becomes of considerable importance. For this reason an effort has been made to facilitate the operations in every way. While the equipment that will be described may seem elaborate, it is justified by the saving of valuable time, and by the dependable results that can be obtained.

I. Description of Spectrophotometric Equipment

LIGHT SOURCE

The light source used for measuring the transmittancy of flour extracts is an adaptation of a commercially available mercury vapor lamp.¹ The reflector provided with the lamp consists of an aluminum hemisphere about 21 cm. in diameter in which the quartz electrode vessel and appurtenances are housed. A shield was constructed for the front of the reflector consisting of a circular, metal piece about 26 cm. in diameter, to which a circular apron about 5.5 cm. wide is attached around the periphery and at right angles to it. An adequate idea of the construction may be obtained from Figure 1. The shield is attached to the reflector by means of short rods about 2.2 cm. long. They conform to the curvature of the rim of the reflector and extend in such a way that they center the shield with respect to the reflector, providing a ventilating space all around. The apron on the reflector extends back (in effect, the reflector extends into the shield but is separated from it by the rods)

¹ Alpine Sun Lamp Manufactured by the Hanovia Chemical and Manufacturing Company



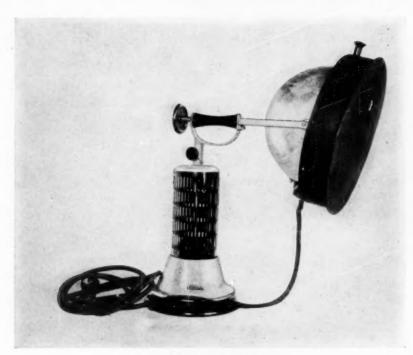


Fig. 1. Mercury vapor light source.

and cuts off much of the stray light. Adequate ventilation for the quartz electrode is important to prevent overheating, and in addition to providing for ventilation in the construction of the light source a stream of air is directed upward from beneath the lamp for additional cooling. This precaution is unnecessary if the lamp is operated for short time intervals, say one hour or less. A rectangular aperture is located in the shield from which the light is taken. The position of this aperture is discussed later. The base of the lamp is weighted with lead, as the attached shield makes the lamp top heavy.

The hemispherical reflector and shield are coated inside with magnesium oxide. To apply this coat it is necessary, of course, to remove the quartz burner. The magnesium oxide may be deposited in the following way, carrying out all operations under a hood. Magnesium metal shavings such as are employed for the Grignard reaction are placed in a wide metal spoon (iron) with a long handle, or in a suitable fire clay container, and ignited with a Bunsen burner. The eyes must be protected from the emitted light by the use of dark yellow glasses. The burning magnesium is held under the surface to be coated and 8 to 10 cm. distant from it. If held too closely yellow magnesium nitride may be deposited. The spoon is moved about to secure a uniform deposit, and the position of the reflector is adjusted as required. The surface must be completely and adequately covered to a depth of 0.5 to 1.0 mm. and the metal beneath must not show through. If the operation has been carried out properly, a beautiful, white, diffusely reflecting surface is obtained which reflects light non-selectively. The shield is coated inside in the same manner. Care must be exercised in replacing the quartz electrode and in handling the light source generally, as the magnesium oxide coating is soft and easily marred.

The aperture through which the light is taken for the spectrophotometer is 14 mm. square and is located on the front shield about
6 cm. above the center. Direct light from the quartz burner is thus
avoided. Instead, the light is taken from an area of the back wall of
the hemisphere that is uniformly illuminated by the diffusely reflected
light coming from the magnesium oxide coated surface inside. This
method of illumination is superior to that in which light is obtained
directly from the mercury vapor arc, as in the latter case lack of brightness uniformity over the entire field, flicker, and other objections may
be serious. The intensity of the illumination secured by the light source
described is considerably enhanced by the reflecting walls of magnesium
oxide. This may be illustrated by considering the following relation
dealing with the intensity of light secured under such conditions,

$$I = \frac{F}{A(1-R)},$$

where I is the total average illumination; F the total light flux generated by the quartz lamp; A the area of the enclosing walls; R the average reflectance of the magnesium oxide coated walls. If the magnesium oxide has been deposited carefully and thoroughly covers the inside surface, a very high reflectance value will be secured. The average direct illumination given by F/A will be increased as the result of multiple reflection, and if a value of R equal to 0.9 or greater is achieved, the total illumination will be increased ten times or more, depending entirely on the value of R. The large ratio of indirect illumination to direct illumination has the further important advantage of contributing to the brightness uniformity of the area from which light is taken for the spectrophotometer.

The mercury vapor light source is supported by a shelf which is adjustable vertically in an angle iron frame, which in turn is fastened securely to and forms an integral part of the table that carries the spectrophotometer with its accessory equipment. An easily removable cover for catching stray light and providing protection from dust may be opened at the top for ventilation when the lamp is operating. The top opening also permits access to the lamp for starting and adjusting. A small sliding door provides an opening through which the light beam enters the spectrophotometer chamber.

Spectrophotometer

The spectrophotometer used is a Koenig-Martens instrument.² The general theory and use of it will not be discussed, as this has already been done in detail by McNicholas (1928). The manner of its use for the determination of carotin will be described in a following section.

The spectrophotometric equipment is illustrated in Figure 2. The spectrophotometer is carried on a stand that rolls in an angle iron track permitting horizontal movement of the instrument in the vertical median plane. This angle iron track is fastened rigidly to a table and is a part of and continuous with the angle iron framework that supports the mercury vapor light source. A suitable condensing lens is used to focus the aperture in the shield of the light source on the illuminating device of the spectrophotometer. The illuminating device projects two parallel beams of light on the collimator slits. Between the collimator slits and the illuminating device is an adjustable stage used to support the cell containing the liquid whose transmittancy is to be measured. To the stage is fastened a mechanical stop made of aluminum. When a cell is placed against this stop it is properly centered and in position for measurements. The cells used are described in Section III.

² Franz Schmidt and Haensch.

A cover for the instrument is provided constructed of pressed wood and is built on a frame in such a way that it may be removed from the table. Light from the source enters through a round aperture that is closed when the instrument is not in use. The cover consists of two compartments separated by a partition that extends down over the instrument and conforms to its shape. The compartment nearest the light source containing the condensing lens system and most of the collimator tube is accessible through a wide door. A small 12 volt electric light operated from a transformer provides illumination when it is needed for the ordinary adjustments. The partition effectively excludes stray light from the source, and permits the operator to read the instrument in comfort. It should be stated that the instrument is used in a room whose windows are provided with double shades, and thus measurements are carried out in a dark room.

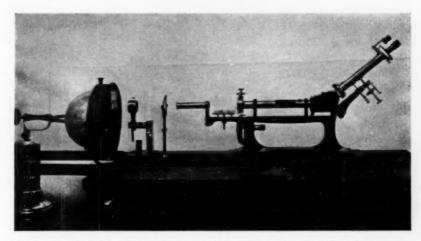


Fig. 2. Koenig-Martëns spectrophotometer with accessory equipment. (Cover is removed.)

The compartment containing the photometer end of the instrument is made accessible by a door that extends the entire width of the cover and may be swung completely out of the way by folding it back over the top. Two small electric lights provide illumination for reading the angular position of the nicol prism and for recording observations. This lighting system consists of two 6-volt lamps operated in series from a transformer through a rheostat that permits latitude in the intensity of the illumination. The lamps are wired in such a way that they may be switched on to operate continuously, or they may be operated momentarily with a bell button used as a switch. The switch, rheostat, and bell button are located conveniently on the left side of the operator just within the compartment.

For illuminating the graduations on the photometer head the light is located above it and a solid glass rod covered with rubber tubing that projects enough to slip over the electric light bulb is suspended from the latter in such a way that it throws a spot of light on the scale where it is read. The intensity is adjusted with the rheostat to provide comfortable vision for reading. No direct light strikes the eye of the observer, and there is very little stray light. To operate the electric light it is only necessary to touch a button, or switch.

For recording observations the other light is attached in an appropriate position on the right side of the compartment. A reflector deflects the light downward on the cards upon which the individual observations are recorded.

II. Preparation of the Flour Extract

In the present procedure 20 gms. of flour is weighed on a Torsion balance having a sensitivity of 15 milligrams. The sample is transferred to a 250 cc. wide-mouthed, glass-stoppered bottle. It is important that high grade bottles with well fitting stoppers be used. To the flour in the bottle 100 cc. of solvent is added by means of a pipette. Cleaner's naphtha or gasoline was used formerly for extraction, but now a mixture consisting of light cleaner's naphtha and absolute alcohol in the proportion of 93 to 7 parts by volume, respectively, is employed. A discussion of various solvents can not be given here and is reserved for a separate paper. It will be sufficient to give the specifications of the cleaner's naphtha known in the trade as "light cleaner's naphtha." It has an initial boiling point of 93.3° C. and an end (maximum) boiling point of 160° C. It is deodorized, and free from gums and sulphur. The specific gravity is not so important, because even with the same initial and end boiling points the specific gravity may vary several points, depending on the source of the oil from which it was made. Thus, cleaner's naphtha from Pennsylvania oils has a higher specific gravity than the same product from other sources. As an example to show merely the range in which the specific gravity falls, a recent lot was 57.5 A.P.I., corresponding to an equivalent density of 0.7487.

A one-liter, Pyrex, florence flask with a heavy ring neck is used to contain the solvent, and to facilitate its addition to the flour a number of measuring units were prepared. Each consists of a rubber stopper that fits the liter flask and bears a 100 cc. pipette, a pressure bulb, and an open hole. The necessary manipulation is obvious. A rack is provided to hold three pipettes while they are emptying into the bottles containing the sample. The measuring units and the rack are illustrated in Figure 3.

The sample and solvent are agitated by a rotary motion in such a way as to secure complete dispersion of the flour, care being taken not to get any of the solvent into the ground glass stopper. Proper manipulation usually achieves complete mixing without resort to a glass rod, but the latter must be used if the flour can not be shaken loose from the bottom of the bottle.

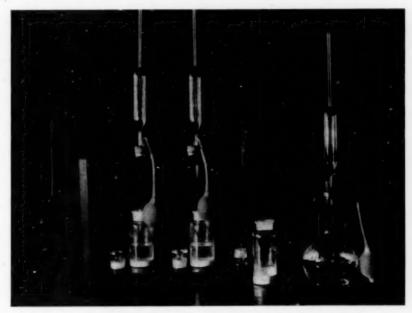


Fig. 3. Device used for measuring 100 cc. aliquots of solvent.

In the conventional procedure employed the samples are agitated at frequent intervals and allowed to stand overnight. They must be protected against direct sunlight. More uniform results will be secured by agitating the samples once more the following morning. After partially settling, the extracts are decanted into lipless centrifuge tubes and securely covered with rubber dam (see Figure 4). They are then whirled in a centrifuge at high speed for 20 minutes. The speed and time necessary are conditioned entirely by the clarity of the resulting extract. For spectrophotometric measurements the extract must be *clear and entirely free from turbidity*.

As the flour particles that have been packed at the bottom of the centrifuge tube are very easily disturbed, the tubes after whirling must be handled with special care. The centrifuge must be allowed to stop of its own accord, i.e., without the application of a brake. Further, ordinary decanting is not permissible and the centrifuged extract must

be withdrawn by means of a siphon tube. This tube is constructed of small-bore glass tubing. The inlet of the siphon is bent in the form of the letter U, and both the inlet and outlet are constricted. In this way siphoning is slow and the flour is not liable to be disturbed. Too elaborate precautions cannot be taken to insure a clear extract. Figure 4 shows a rack used for facilitating the routine handling of a large number of flour extracts and containing a number of centrifuge tubes that may be siphoned simultaneously.



Fig. 4. Siphon units for removing clear centrifuged flour extracts.

While most flours may be extracted and centrifuged in the manner described, some samples will not yield an extract that has the necessary clarity. Space will not permit a discussion of turbidity in detail. It was this difficulty with some samples that led to the use of the alundum filtration procedure described in a previous paper (Ferrari and Bailey, 1929a).

III. Spectrophotometric Procedure for the Quantitative Determination of the Carotinoid Pigments of Wheat Flour

Spectrophotometric examination of the flour extract is carried out with the Koenig-Martens spectrophotometer described in Section I using a wave length of 435.8 m μ from the mercury vapor light source. For this purpose a special type of double compartment cell ³ was designed that has some advantages over the screw-cap type. Several of these cells are illustrated in Figure 5, and detailed discussion of their construction appears unnecessary. The solvent is placed in one compartment, and the pigmented extract in the other. A glass cover is used

³ Made to order.

to retard evaporation. Several sizes of cells are used, but chiefly those 5 and 9 cm. long. The latter is the longest cell of even centimeter length that will fit on the stage of the Koenig-Martens spectrophotometer equipped with the small illuminating device.

In carrying out the determination of transmittancy with the Koenig-Martens instrument angles of match can be obtained in each of the four quadrants. For the utmost accuracy readings should be made in all four quadrants and averaged. However, McNicholas (1928) has shown that in routine work the use of a single quadrant leads to only very small errors. In practice, then, readings are made in the first quadrant only.

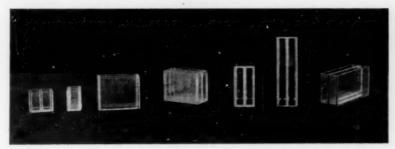


Fig. 5. Double compartment cells used for transmittancy measurements.

After the wave length scale has been adjusted for $435.8\,\mathrm{m}\mu$ five readings are made, first with the pigmented extract in one beam, and then the cell is shifted and five readings are made with the extract in the other beam. These readings are averaged. The larger angular reading is designated by θ_1 and the smaller by θ_2 . The transmittancy of the extract is then given by the relation $T = \cot \theta_1 \tan \theta_2$. For this calculation a special slide rule 4 having a cotangent and tangent scale is used.

In carrying out the measurement of transmittancy as described, the Martens type of photometer compensates for any polarization due to the substance examined, and further compensates for any deviation of the match point from 45° . The former is a decided advantage in the examination of extracts containing carotin, the a form of which is optically active.

The concentration of the carotinoid pigments in the extract is expressed as carotin. The relation between transmittancy and carotin concentration has been discussed in a previous paper (Ferrari and Bailey, 1929). Tables have been prepared giving the concentration of

⁴ This rule was designed by the late I. G. Priest, at the U. S. Bureau of Standards, and was made to order by Keuffel and Esser Co., Hoboken, N. J.

carotin in the extract in milligrams per liter for transmittancies from 0.001 to 0.999 in steps of 0.001. The concentration of carotin in the flour is calculated from the determined milligrams of carotin per liter of extract and the quantity of flour and solvent employed. As 20 gms. of flour and 100 cc. of solvent are used in the conventional method we employ, it follows that for the conditions named the carotin in the extract must be divided by 0.2 or multiplied by 5.0.

Summary

Spectrophotometric equipment for quantitatively determining the carotinoid pigments of wheat flour is described. Construction of the mercury vapor light source is detailed, and a short discussion of the quality of illumination and light intensity is given. The Koenig-Martens spectrophotometer and accessory equipment used in this laboratory are described.

A flour extract is prepared with a mixture of light cleaner's naphtha and absolute alcohol in the proportion of 93 to 7 parts by volume, respectively. The conventional procedure described requires standing overnight, followed by centrifuging at high speed. Facilities for the routine handling of samples, including a convenient double compartment cell in which transmittancy measurements are made, is described. Readings are made with a Koenig-Martens spectrophotometer at wave length 435.8 m_µ, first with the pigmented extract in one beam, and then in the other, using the first quadrant of the circular scale on the photometer. The larger angular reading is designated by θ_1 and the smaller by θ_2 . Transmittancy is calculated with a special slide rule having a cotangent and tangent scale, or it may be calculated from the relation $T = \cot \theta_1 \tan \theta_2$. Transmittancy is related to carotin concentration and the results are expressed as parts of carotin per million parts of flour.

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THE VITAMIN B AND G CONTENT OF WHEAT GERM, RICE POLISHINGS, COTTONSEED FLOUR, AND THE RESIDUE FROM FERMENTED RYE GRAINS

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Introduction

The importance of including liberal amounts of vitamins B and G in the diet at all times has been given new emphasis during the last few years. Both of these vitamins are essential for growth of the young and well-being of the adult, and vitamin B is especially needed by the mother during pregnancy and lactation.

Although vitamins B and G occur in a wide variety of foods in relatively small amounts only a few concentrated sources are known. The germ and pericarp portions of whole grains are among the most important. Since the germ tends to become rancid and the bran detracts from the appearance of the final product, these are generally removed when the grain is milled and relegated to animal feeds. Oftentimes the food constituents lost in this way are the very ones lacking in the diets of those who use large quantities of highly milled grains and prepared cereals.

The feasibility of using these milling by-products in human dietaries was investigated in the U. S. Bureau of Home Economics. In the course of a dietary study which this bureau carried out in South Carolina (Stiebeling and Munsell, 1932), wheat germ was found to be a palatable food and also to be valuable in preventing pellagra. Coincident with this study several products were tested for their vitamin B and vitamin G contents. The report given here covers the vitamin studies. Tests were made on four samples of wheat germ obtained from various mills, and two samples of rice polishings. A cottonseed flour and a flour made from the residue of fermented rye grain were also tested at this time and the results are included here since both flours were found to be significant sources of the two vitamins. Results obtained with whole wheat and dry yeast are included in order to have familiar foods to use as a basis of comparison.

Studies with Wheat Germ

Numerous investigators have reported data on the water-soluble B content of the wheat kernel. Osborne and Mendel (1919), Hunt (1928), and Steenbock, et al. (1923), determined the percentage of whole wheat necessary in the diet to supply sufficient vitamin B complex for growth of the rat. The values obtained by these investigators vary widely. Ingestion of excreta by the animals and variation in the vitamin content of the grain itself may account for the different results obtained. The latter explanation is supported by the work of Bell and Mendel (1922) who showed that Marquis spring wheat was much richer in the vitamin B complex than was Minnesota winter wheat.

Osborne and Mendel (1919), and Bell and Mendel (1922) determined the amount of the vitamin B complex in the different parts of the wheat kernel. According to Bell and Mendel (1922) the germ portion is several times richer than the endosperm in the vitamin B complex. They call attention to the fact, however, that the germ constitutes only about 2% of the total weight of the wheat kernel and contains not more than one-sixth of the total quantity of the vitamin present in the whole grain.

According to Hunt (1928), Aykroyd and Roscoe (1929), and Sherman and Axtmayer (1927), whole wheat is richer in vitamin B than in vitamin G. Hetler, Meyer, and Husseman (1931) conclude that although 25% of winter wheat supplied enough vitamin G for normal growth, 50% is required in the diet to furnish enough vitamin G. Mitchell (1930–31) using the paired feeding method, shows that between 50% and 55% of whole wheat is required to furnish adequate vitamin B.

According to Cramer and Mottram (1927) wheat germ is as rich in vitamin B as yeast. They express the relative vitamin B potency of the different parts of the wheat kernel as follows: Germ 100, middlings 50, bran 33, and patent flour 0. Roscoe (1931) states that if brewers' yeast is given a rating of 100 on the basis of its vitamin B and G content, wheat germ then has a relative value of 50 as a source of vitamin B, and from 5 to 10 as a source of vitamin G.

Experimental

Four samples of commercial wheat germ from four different mills were tested for their vitamin B and vitamin G potency. The wheat germ was received from the mills in cloth bags, transferred to glass jars, sealed, and kept in the refrigerator until used. Sample 1 was milled from a blend of 60% hard red wheat and 40% hard white. Different lots of wheat germ from this mill were used for the vitamin B and vitamin G assays, but all were taken from wheats blended and milled

in the same manner. Sample 4 was described as "2 Red 59 pound soft red winter wheat." No information is available about the other two samples.

Methods Used to Determine Vitamin Content

The tests for vitamin B (B_1) were made by the following method worked out in this laboratory. Rats 28 or 29 days old, of known dietary history, were put on a basal diet consisting of purified casein, 18%; Osborne and Mendel salt mixture, 4%; starch, 58%; butterfat, 8%; cod liver oil, 2%; and yeast (autoclaved for 4 hours at 20 pounds pressure), 10%. Following the recommendations of Chase and Sherman (1931) the rats were kept on this basal diet for a period of two weeks before the actual tests were made since that is the average length of time required to deplete the body store of vitamin B. At the end of this depletion period the material to be tested was either fed as a supplement three times weekly, or incorporated into the basal diet, replacing equivalent percentages of the starch. In general, a group of eight rats, containing four males and four females, was used for each of the levels of feeding. At the end of the 8-week test period all rats were killed and autopsied.

The technic used in the vitamin G tests was that of Bourguin and Sherman (1931), except that an alcoholic extract of white corn was used as a source of vitamin B, instead of an alcoholic extract of wheat. This preparation, which has been in use for some time in this laboratory, has been found to contain no appreciable amount of vitamin G. The basal diet consisted of purified casein, 18%; Osborne and Mendel salt mixture, 4%; butterfat, 8%; cod-liver oil, 2%; and the extract from 90 gms. of white corn plus cornstarch to make 100%. The rats were kept on the basal diet for a preliminary period of two weeks to deplete them of some of their body store of vitamin G. As in the case of vitamin B, groups of eight rats containing four males and four females were fed the test food for an 8-week period when they were killed and autopsied. Foods to be tested for vitamin G were either weighed and fed as a separate supplement three times a week or, in a few cases, incorporated into the basal diet by replacing an equivalent quantity of starch.

The results obtained with wheat germ are tabulated in Tables I and II, and the differences in growth resulting from feeding equal quantities of the various samples of wheat germ are shown in Figures 1 and 2. The wheat germ samples were evaluated according to the number of units of vitamin B and vitamin G they contained, a unit in each case being that amount which, when fed daily, induces a gain in weight of 25 gms. in eight weeks. In terms of units per gram the values for the vitamin

TABLE I WHEAT GERM AS A SOURCE OF VITAMIN B

Wheat germ			Average	Aver-	Average	Estimated quantity	Units		
Sample number	Quantity fed daily 6 times per week	Rats used in test	weight at end of depletion period	age gain in weight during 8 weeks	devi- ation of gain in weight ¹	of wheat germ to give 25 gms. gain in 8 weeks	(Sherman) per gram		
	Gms.	No.	Gms.	Gms.	Gms.	Gms.	No		
	0.125	8	73.4	31.9	5.9				
1	0.25	8	72.6	66.5	7.2	0.10	10.0		
	0.5	8	71.8	99.5	16.8				
	0.125	8	68.9	-2.3	6.0				
4	0.25	8	67.5	34.0	7.2	0.22	4.5		
	0.50	8	67.4	65.0	11.8				
	0.125	8	69.1	18.6	9.9				
5	0.25	8	70.5	51.0	5.0	0.15	6.7		
	0.5	8	68.6	91.0	15.8				
	0.125	8	65.9	9.1	8.6				
5a	0.25	8	66.3	39.0	5.8	0.19	5.3		
	0.5	8	66.9	72.5	10.4				
0 7 63.4					All died before end of experimenta				

¹ The average deviation has been calculated for each group as a whole since the number of males and females is too small to warrant the calculation of a standard deviation of the mean gain in weight of each sex.

TABLE II WHEAT GERM AS A SOURCE OF VITAMIN G

Wheat germ			A	A	Α	Estimated	TT
Sample number	Quantity fed daily 6 times per week	Rats used in test	Average weight at end of depletion period	Average gain in weight during 8 weeks	Average devi- ation of gain in weight ³	quantity of wheat germ to give 25 gms. gain in 8 weeks	Units (Sher- man) per gram
	Gms.	No.	Gms.	Gms.	Gms.	Gms.	No.
	0.5	8	66.3	22.9	4.1		
1	1.0	8	66.6	41.8	8.0	0.57	1.8
	1.5	6	67.7	53.7	3.2		
	0.5	8	66.5	29.4	6.6		
4	1.0	8 8 8	65.6	41.9	11.6	0.43	2.3
	1.5	8	65.8	59.3	13.5		
	0.125	8	64.6	15.9	2.9		
5	0.25	8	65.4	24.1	4.1	0.26	3.8
	0.50	8	65.6	39.4	4.6		
	1.0	8	65.0	57.5	15.1		
	0.5	8	60.0	31.3	6.6		
5a	1.0	8	60.3	53.6	7.5	0.39	2.6
	1.5	8	60.8	67.5	12.0		
	0	9	58.5	3.8	7.5		

¹ See footnote 1, Table I.

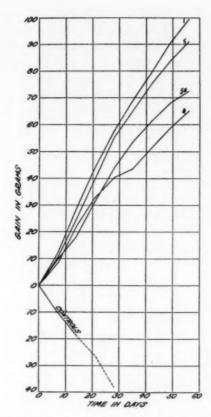


Fig. 1. Average gains in weight of four groups of rats fed 0.5 gm. of wheat germ daily as a source of vitamin B. A different wheat germ sample was fed each group. The numbers on the curves are the identification numbers for the wheat germ samples.

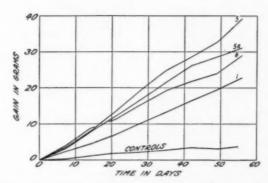


Fig. 2. Average gains in weight of four groups of rats fed 0.5 gm. of wheat germ daily as a source of vitamin G. A different wheat germ sample was fed each group. The numbers on the curves are the identification numbers for the wheat germ samples.

B content of the four samples were 10.0, 4.5, 6.7, and 5.3 respectively, and for vitamin G 1.8, 2.3, 3.8, and 2.6. From these results it appears that commercial wheat germ is a rich and fairly constant source of these vitamins. In the case of samples 2, 4, and 5a, where the vitamin B and vitamin G tests were made on the same lots, the amount of vitamin G seems to vary directly with the concentration of vitamin B, i.e., high vitamin G is associated with high vitamin B content, and low vitamin G with low vitamin B.

Studies with Whole Wheat

The whole wheat tested was taken from different lots of soft winter wheat received in the U. S. Bureau of Home Economics over a period of several months. The same technic was used here as in the tests on wheat germ except that in the vitamin G determinations the wheat was incorporated in the diet at levels at 25%, 35%, and 50%. The results, summarized in Table III, show that the wheat contained 1.5 units of

TABLE III
Whole Wheat as a Source of Vitamins B and G

Quantity fed	Rats used in test	Average weight at end of depletion period	Average gain in weight during 8 weeks	Average devi- ation of gain in weight ¹	Estimated quantity of wheat to give 25 gms. gain in 8 weeks	Units (Sher- man) per gram
	No.	Gms.	Gms.	Gms.	Gms.	No.
		As Source	e of Vitami	in B		
Daily, 6 times						
per week	0	(0.0	* *	11.6		
0.375 gm.	8	69.0	7.5	11.6	0.70	4 11
0.75 gm.	8	68.3	27.9	5.8	0.69	1.5
1.5 gm.	8	68.8	68.1	8.4		
		As Source	e of Vitami	in G		
Per cent of diet 25% (Average daily	8	59.6	35.6	9.9		
intake 1.7 gms.) 35%	8	58.9	41.6	9.0	1.2	0.8
(Average daily intake 2.4 gms.) 50% (Average daily intake 4.1 gms.)	8	60.3	56.8	16.3		

¹ See footnote 1, Table I.

vitamin B and 0.8 units of vitamin G per gram and is a relatively poor source of each of these vitamins. The maximum amount fed, approximately 20% as a source of vitamin B and 50% as a source of vitamin G, did not supply adequate amounts of these factors for optimal growth.

Since no values for the vitamin content of the germ portion of this particular wheat are available no statement can be made as to the distribution of the vitamins in the whole kernel. However, if the average of the values obtained for the four wheat germ samples is used for comparison, this wheat is roughly one-fifth as rich in vitamin B and one-third as rich in vitamin G as the wheat germ.

Studies with Rice Polishings

Judged by the effect on lactation, rice polishings, according to Sure (1928), contain an appreciable amount of vitamin B but are deficient in vitamin G. Also, according to Munsell (1929), rice polishings are a good source of vitamin B but contain very little vitamin G. Hetler, Meyer, and Husseman (1931), on the other hand, report that they may contain considerable amounts of vitamin G. Meyer and Smith (1930–31) conclude that 50% of autoclaved rice polishings contain almost enough vitamin G for normal growth.

Two samples of rice polishings were tested. The results, summarized in Table IV, show that rice polishings are a relatively rich source of vitamin B and a poor source of vitamin G. These findings are in agreement with the majority of those reported by other investigators. There was little apparent difference in the values obtained with the two samples.

TABLE IV
RICE POLISHINGS AS A SOURCE OF VITAMINS B AND G

Rice polishings			A	A	A	Estimated	T 7 - 14 -
Sample number	Quantity fed daily 6 times per week	Rats used in test	Average weight at end of depletion period	Average gain in weight during 8 weeks	devia- tion of gain in	quantity of rice polish- ings to give 25 gms. gain in 8 weeks	(Sher- man)
	Gms.	No.	Gms.	Gms.	Gms.	Gms.	No.
		L.	1s Source o	of Vitamin	B		
	0.06	4	69.2	- 1.5	6.0		
2 .	0.125	6	72.1	18.5	11.8	0.15	6.7
	0.25	6	66.5	53.5	3.8		
	0.06	4	71.0	-15.8	4.4		
3.	0.125	4	69.0	1.5	6.8	0.20	5.0
	0.25	4	67.8	39.5	4.5		
		A	Is Source of	of Vitamin	G		
	0.5	4	65.2	13.5	5.5		
2	1.0	4	67.0	23.2	6.1	1.00	1.0
	1.5	4	65.2	30.5	2.5		
	0.5	4	68.8	6.0	3.5		
3	1.0	4	61.5	13.2	6.8	1.85	0.5
	1.5	4	67.5	19.8	1.4		-10

¹ See footnote 1, Table I.

Studies with Cottonseed Flour

Very little is found in the literature concerning the vitamin content of cottonseed flour. According to Macy and Mendel (1920) the toxic effects of cottonseed are not due to lack of the water-soluble vitamins (B complex). Richardson and Green (1917) state that the aqueous extract of 50% of cottonseed flour in the diet furnishes sufficient of the B complex for normal growth.

One sample of cottonseed flour (Allison) was tested for its vitamin B and vitamin G content. The results of these studies, given in Table V, show that cottonseed flour is an excellent source of vitamin B and a good source of vitamin G. No evidence of toxicity was observed even with rats receiving 30% in the diet for a period of six months.

TABLE V

COTTONSEED FLOUR AS A SOURCE OF VITAMINS B AND G

Quantity fed	Rats used in test	Average weight at end of depletion period	Average gain in weight during 8 weeks	Average devi- ation of gain in weight 1	Estimated quantity of cottonseed flour to give 25 gms. gain in 8 weeks	Units (Sherman) per gram
	No.	Gms. As Sourc	Gms. e of Vitam	Gms.	Gms.	No.
Daily, 6 times						
per week	0	601	7.9	5.1		
0.125 gm. 0.17 gm.	8	68.1 67.0	16.8	5.4	0.21	4.7
0.21 gm.	8 8 7	64.7	24.7	5.1	0.21	7.8
0.25 gm.	8	66.9	29.3	5.5		
		As Source	e of Vitam	in G		
Per cent of diet 20%	16	60.8	65.1	16.8		
(Average daily						
intake 1.55 gms.)	8	61.5	78.4	26.0	0.6	1.7
(Average daily intake 2.26 gms.)						

¹ See footnote 1, Table I.

Studies with Residue from Fermented Rye Grain

One sample of a flour made from the residue left after the distillation of alcohol from fermented rye grain was tested for its vitamin B value. This material was incorporated in the basal diet at 20% and 30% levels. Of the twelve rats on the lower level only two survived a nine-week feeding period and one of these was polyneuritic when killed at the end of the tenth week. The twelve rats fed 30% of the flour made an average gain in weight of 25.3 gms. in eight weeks. The

flour, therefore, contained about 0.4 Sherman unit of vitamin B per gram, which is a small but appreciable amount of this factor. A limited number of tests indicated that this flour has a fairly high content of vitamin G.

Since, at the time these studies were made, there was no generally accepted standard unit for measuring vitamin B and vitamin G content, it was decided to evaluate the vitamin content of the substances investigated in terms of dry powdered yeast. Accordingly, three lots of dried brewers' yeast were composited and assayed. The data from these studies are given in Table VI. The values in terms of units check well with the vitamin G content as determined by Aykroyd and Roscoe (1929) and Quinn, Whalen, and Hartley (1930). The former workers give a value of from 5 to 10 of their units (2½ to 3 times the Sherman-Bourquin unit) for dried yeast while the latter report from 10 to 15 Sherman-Bourquin units per gram.

TABLE VI
DRIED BREWERS' YEAST AS A SOURCE OF VITAMINS B AND G

Quantity fed daily 6 times per week	Rats used in test	Average weight at end of depletion period	Average gain in weight during 8 weeks	Average deviation of gain in weight 1	Estimated quantity of yeast to give 25 gms. gain in 8 weeks	Units (Sherman) per gram
Gms.	No.	Gms.	Gms.	Gms.	Gms.	No.
		As So	urce of Vit	amin B		
0.06	8	69.6	10.6	7.1		
0.09	8	68.6	23.5	4.4	0.09	11.1
0.125	8	67.6	45.6	6.8		
0.25	8	66.1	69.5	7.4		
		As So	urce of Vit	amin G		
0.06	8	64.8	26.6	2.6		
0.125	8	62.8	44.0	6.0	0.06	16.7
0.25	8 8 8	62.8	66.6	8.9		
0.50	8	63.8	95.0	17.0		

¹ See footnote 1, Table I.

In Table VII the vitamin B and vitamin G contents of the various substances tested are summarized and compared with yeast given an arbitrary value of 100. The vitamin B values for wheat and wheat germ check well with those found by Plimmer, et al. (1931), from maintenance tests with pigeons. His values are: 100 for dried yeast, 62 for wheat germ, and 8 to 10 for wheat. Our results are also in good agreement with the results of Roscoe (1931) which were mentioned earlier.

TABLE VII

VITAMIN B AND G CONTENT OF THE VARIOUS SUBSTANCES TESTED COMPARED WITH DRIED YEAST AS A SOURCE OF THESE TWO VITAMINS

		lues in terms Sherman)	Comparison on basis of yeast as 100		
Substance	Vitamin B	Vitamin G	Vitamin B	Vitamin G	
Yeast	11	17	100	100	
Wheat germ	7	3	60	15	
Wheat	1.5	1	13	5	
Rice polishings	6	1	53	4.5	
Cottonseed flour Residue from fermented	5	2	43	10	
rye grain	0.4	_	4		

Summary

Samples of wheat germ, cottonseed flour, and rice polishings have been tested and found to be excellent sources of vitamin B. These three substances all contained approximately one-half as much of the antineuritic factor as did a composite sample of dried yeast. As a source of vitamin G they differed widely.

Wheat germ was the richest of the three substances, containing about one-sixth as much vitamin G as did the yeast. Cottonseed flour was found to have about one-tenth as much of this factor as yeast, while rice polishings had only about one-twentieth.

Whole wheat (soft winter) was found to be a relatively poor source of both vitamins B and G. The flour made from the residue from fermented rye grain contained a very small but appreciable amount of vitamin B.

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THE HYDRATION CAPACITY OF STARCH 1

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Introduction

Various attempts have been made to measure the degree of solvation of the micelles of lyophilic colloids. It is generally recognized that viscometric technic is perhaps the simplest method which can be used, but the interpretation of the data in terms of degree of solvation of the micelles has presented difficulties. The ordinary Poiseuille formula,

$$\eta = \frac{\pi r^4 pt}{8 \, lV},\tag{1}$$

with the concomitant assumption of an approximately straight line relationship between viscosity and concentration, holds fairly well for true solutions but fails when applied to lyophilic sols.

Einstein (1906) proposed the formula,

$$\eta' = \eta (1 + K\phi), \tag{2}$$

where η' = the viscosity of the lyophilic sol,

 η = the viscosity of the dispersions medium,

 ϕ = the ratio of space occupied by the disperse phase (solvated micelles) to the total volume of the system,

K = a constant.

This formula expressed in terms of relative viscosity becomes

$$\frac{\eta}{\eta_0} = 1 + K\phi. \tag{3}$$

Einstein suggested a value of 1.0 for the constant K but in later calculations (Einstein, 1911) gave this constant a value of 2.5.

Hatschek (1910) proposed the formula,

$$\frac{\eta}{\eta_0} = 1 + 4.5 \,\phi,\tag{4}$$

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but has recognized (Hatschek, 1913) that this is only a rough approximation. Later Hatschek (1920) proposed the formula,

$$\frac{\eta}{\eta_0} = \frac{1}{1 - \sqrt[3]{\phi}},\tag{5}$$

and found that it held well for the viscosity of suspensions of blood corpuscles. Various workers have, however, experienced difficulties in applying the suggested formulae to miscellaneous lyophilic sols of widely differing concentration.

More recently Kunitz (1926) has proposed the formula,

$$\frac{\eta}{\eta_0} = \frac{1 + 0.5 \,\phi}{(1 - \phi)^4},\tag{6}$$

and finds that it holds well for such diverse systems as sugar solutions, Oden's sulfur hydrosols, glycogen and casein hydrosols, and sols of rubber in various organic liquids.

Freeman and Gortner (1932) using Kunitz's formula (6) found that the gum of wheat flour had an approximately constant degree of hydration of about 800% in hydrosols ranging from 2.01% to 7.33% concentration. Accordingly, it appeared desirable to see whether or not this formula would yield valuable information when appplied to a study of starch hydrosols.

Experimental

Solution of Equation (6). Formula (6) is a fourth degree equation and as such is not capable of direct solution. It is accordingly necessary to plot the theoretical curve on cross section paper and use this theoretical graph for the determination of the per cent of the sol which is occupied by the disperse phase at the values of viscosity which are experimentally determined. Accordingly the theoretical values of relative viscosity were calculated for ϕ values ranging from 10% to 80%. In order to assist others who may wish to plot theoretical reference curves these solutions of equation (6) are given in Table I.

The Hydration Capacity of Heat gelatinized Starches from Various Botanical Sources.—Samec and Haerdtl (1920) have determined the relative viscosities of starches derived from different botanical sources. A part of these data, with calculations of the "volume occupied by one gram of starch" in the heat-gelatinized sol is given in Table II.

The Hydration of Heat-gelatinized Wheat Starch from Various Wheat Varieties. Rask and Alsberg (1924) studied the viscosities of sols of heat-gelatinized wheat starch from various commercial wheat

TABLE I

Value of Relative Viscosity (η/η_0) and Volume of Sol. (ϕ) Occupied by the Disperse Phase for Plotting the Curve of the Equation $\eta_r = \frac{1+0.5\,\phi}{(1-\phi)^4}$

φ	η_r	φ	η_r
0	1.000	60	50.781
10	1.600	62	62.830
20	2.686	64	78.589
30	4.790	66	99.526
40	9.274	68	127.807
42	10.692	70	166.677
44	12.405	72	221.30
48	16.959	74	299.80
48 50	20.000	76	415.94
52	23.736	78	593.37
54	28.364	80	875.00
56	34.151	30	0,0,00

varieties. Their data together with calculations of relative viscosity and the "volume occupied by one gram of the starch" in these sols are given in Table III, and the changes in volume with changes in concentration of the sol are shown graphically in Figures 1 and 2.

The Retrogression of Heat-gelatinized Starch. It is generally recognized that starch pastes retrograde on standing. Samec and Hoefft (1913) have presented viscosity data dealing with this question. A calculation of the changes in hydration which their data show is given in Table IV.

The Effect of Duration of Heating on the Hydration Capacity of Heat-gelatinized Starch. Samec and Hoefft (1913), Samec and Jenčič (1915), and Samec and Kavčič (Samec, 1927, p. 197) studied the effect

TABLE II

THE HYDRATION AT 25° C. OF STARCHES FROM VARIOUS BOTANICAL SOURCES (All samples gelatinized in 2% concentration for one hour at 120° C. viscosities on 1% sols. at 25° C. Calculation from data of Samec and Haerdtl)

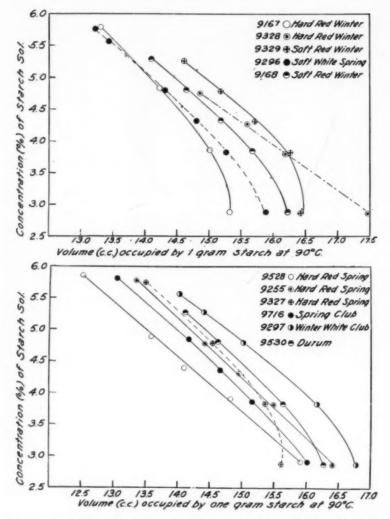
	η_r	φ	Volume occupied by one gram
		P.ct.	Cc.
Potato (fat extracted, Kahlbaum)	6.63	35.00	35.00
Potato (ordinary)	5.05	30.75	30.75
Meadow-saffron (Colchicum autumnale)	3.34	28.33	28.33
Arrowroot (Maranta arundinacea)	3.13	22.75	22.75
Cassava (Manihot utilissima)	2.72	20.20	20.20
Zedoary (Curcuma Zedoaria)	2.59	19.40	19.40
Horse-chestnut (Aesculus hippocastanum)	2.47	18.50	18.50
Wheat (Triticum vulgare)	2.10	15.50	15.50
Glutinous rice (Oryza glutinosa)	1.96	14.50	14.50
Maize (Zea mays)	1.60	10.25	10.25
Rice	1.48	8.5	8.5

TABLE III

The Hydration at 90° C. of Heat-gelatinized Wheat Starch (Calculations from the data of Rask and Alsberg)

Sample number and type	Concen- tration of starch	Viscosity	Relative viscosity	Volume occupied by one gram of starch		
	P.ct.	Centipoise		P.ct.	Cc.	
9167	2.89	4.0	12.66	44.3	15.33	
Hard red winter	3.86	13.0	41.14	57.93	15.01	
	4.83	45.0	142.4	68.75	14.23	
	5.79	158.0	500.0	77.06	13.31	
9168	2.89	4.9	15.51	46.9	16.23	
Soft red winter	3.85	16.6	52.53	60.37	15.68	
	4.33	30.5	96.52	65.72	15.18	
	4.81	56.0	177.2	70.5	14.65	
	5.29	104.2	329.7	74.58	14.10	
9255	2.87	4.8	15.12	47.1	16.41	
Hard red spring	3.83	15.0	47.47	59.34	15.49	
	4.31	26.0	82.28	64.42	14.95	
	4.79	46.5	147.2	69.13	14.43	
	5.74	146.5	464.0	76.63	13.35	
9296	2.88	4.5	14.24	45.8	15.90	
Soft white spring	3.84	14.0	44.30	58.63	15.27	
	4.32	25.0	79.11	64.03	14.82	
	4.80	44.5	140.8	68.72	14.32	
	5.57	109.0	345.0	74.85	13.44	
	5.76	135.5	429.0	76.17	13.22	
9297	2.88	5.5	17.41	48.32	16.78	
White club winter	3.84	20.0	63.29	62.10	16.17	
	4.80	70.5	223.1	72.07	15.01	
	5.28	132.0	417.7	76.03	14.40	
	5.57	188.0	595.0	78.10	14.02	
9327	2.88	4.2	13.29	44.95	15.61	
Hard red spring	3.84	14.5	45.89	59.00	15.36	
	4.79	50.0	158.2	69.65	14.54	
	5.75	172.0	544.3	77.56	13.49	
9328	2.85	6.2	19.62	49.8	17.47	
Hard red winter	3.80	18.8	59.49	61.50	16.18	
	4.27	33.0	104.4	66.60	15.60	
	4.75	57.8	182.9	70.66	14.87	
9329	2.87	5.0	15.82	47.14	16.43	
Soft red winter	3.83	20.5	64.87	62.28	16.26	
	4.31	39.0	123.4	67.75	15.72	
	4.79	77.5	245.3	72.70	15.18	
0.530	5.27	157.0	496.8	77.05	14.62	
9528	2.93	4.8	15.19	46.63	15.91	
Marquis	3.91	13.0	41.14	57.93	14.82	
	4.40	20.0	63.29	62.05	14.10	
	4.89	32.0	101.3	66.34	13.57	
0520	5.86	84.5	267.4	73.30	12.51	
9530	2.88	4.9	15.51	46.90	16.28	
Durum	3.84	16.2	51.27	60.0	15.63	
	4.81	55.0	174.0	70.30	14.62	
0717	5.28	103.0	325.9	74.50	14.11	
9716	2.91	4.8	15.19	46.63	16.02	
Dicklow Club	3.87	14.0	44.30	58.68	15.16	
	4.37	25.0	79.1	64.04	14.65	
	4.85	44.5	140.8	68.71	14.17	
	5.82	131.0	414.6	75.98	13.05	

on viscosity of autoclaving potato and wheat starches at 120° C. for different periods of time. Their data together with changes in hydration capacity are shown in Tables V and VI.



Figs. 1 and 2. Showing the volume occupied at 90° C. by one gram of heat-gelatinized wheat starch for various wheat sorts, as a function of the concentration of the starch sol.

The Hydration Capacity of Cold-gelatinized Wheat Starches. Wo. Ostwald and Frenkel (1927) have shown that raw starch may be geiatinized at room temperature by the addition of solutions of certain electrolytes and non-electrolytes. Mangels (1932) has applied their technic to a viscometric study of a series of starches from various wheat sorts.

TABLE IV

RETROGRESSION OF STARCH

Potato starch gelatinized in a 4% concentration for 2 hours at 120° C., then part was diluted to a 1% concentration and part to a 2% concentration and the various concentrations were allowed to stand at constant temperature for a varying number of days. Viscosity determined at 25° C. on a 1% sol. (Calculations from the data of Samec and Hoefft.)

ITOIII LIK	c data OI		tored at 15° C.	St	ored at 35° C.	St	ored at 58° C.
Con- centration of store gelatinize stock	d Time	η_r	φ (%) and vol- ume occupied by one gram of starch	ηr	φ (%) and vol- ume occupied by one gram of starch	ητ	φ (%) and vol- ume occupied by one gram of starch
P.ct.	Days		Cc.		Cc.		Cc.
1	Ő	3.15	22.85	3.15	22.85	3.15	22.85
1	1	3.10	22.50	3.09	22.48	3.03	22.15
1	4	2.95	21.75	2.95	21.75	2.53	19.00
1	11	2.72	20.25	2.79	20.75	1.89	13.50
1	20	2.46	18.45	2.65	19.75	1.55	9.50
1	31	2.14	15.90	2.54	19.00	1.45	8.00
2	0	3.15	22.85	3.15	22.85	3.15	22.85
2 2 2 2 2 2 4	1	3.16	22.90	3.06	22.35	2.93	21.60
2	4	3.08	22.45	2.97	21.80		
2	11	2.88	21.25	2.96	21.78		
2	20	2.72	20.25	2.95	21.75		
. 2	31	2.53	19.00	2.95	21.75		
* 4	0	3.15	22.85	3.15	22.85	3.15	22.85
4	1	2.92	21.50	3.12	22.60	3.17	23.00
4	4			2.95	21.75		
4	11			2.34	17.50	2.58	19.25
4	20			1.83	12.85	2.44	18.25
4	31	2.26	16.88	1.71	11.56		

TABLE V

THE EFFECT OF DURATION OF HEATING DURING GELATINIZATION ON THE HYDRA-

TION OF POTATO AND WHEAT STARCHES
The potato starch was gelatinized in 1%, 2%, and 4% concentrations at 120°.
All viscosities were run on 1% sols. at 25° C. (Calculations from the data of Samec and Hoefft, and Samec and Kavčič.)

	S	1% potato tarch auto- ved at 120° C.	S	2% potato tarch auto- ved at 120° C.	S	4% potato starch auto- ved at 120° C.		Wheat starch auto- ved at 120° C.
Length of time in autoclave	ηγ	φ (%) and vol. occupied by one gram of starch		φ (%) and vol. occupied by one gram of starch	ητ	φ (%) and vol. occupied by one gram of starch	ŋr	φ (%) and vol. occupied by one gram of starch
Hrs.		Cc.		Cc.		Cc.		Cc.
0.25	31.69	55.23	11.92		9.34		Manageria.	_
0.50	18.52	49.10	9.45	40.25	7.47	36.75	2.52	18.85
1	6.08	33.65	5.91	33.20	5.40	31.80	_	German
2	2.11	15.60	3.22	23.25	2.84	21.00	_	-
2 3	1.40	7.50	1.70	11.45	1.87	13.40	1.88	13.50
4	1.28	5.00	1.39	7.40	1.44	7.90	-	-
5	1.27	4.90	1.27	4.90	_	_	1.72	11.75

TABLE VI

THE EFFECT OF TEMPERATURE OF GELATINIZATION AND THE DURATION OF HEATING ON THE HYDRATION OF POTATO STARCH

The starch was gelatinized in a 2% sol. and later diluted to a 1% sol. for viscosity determinations. Viscosities at 25° C. (Calculations from the data of Samec and Jenčič.)

		Potato starch oclaved at 120° C.	Potato starch autoclaved at 135° C.		Potato starch autoclaved at 150° C.		
Length of time in autoclave	η_r	(%) and volume occupied by one gram of starch	η_r	(%) and volume occupied by one gram of starch	η_r	occupied by one gram of starch	
Hrs.		Cc.		Cc.		Cc.	
1	7.16	36.10	3.23	23.30	2.23	16.60	
2	3.75	25.75	_	_	_	Comment.	
3	_	_	2.12	15.75	1.38	6.90	
4	2.48	18.60	-	-	_	-	
6	1.70	11.50	1.85	13.10	1.10	1.70	
8	1.46	8.25			_	_	

Certain of Mangel's data, together with calculations of the volume occupied by one gram of starch in the gelatinized sols, are given in Tables VII to XI inclusive. Graphs calculated from the data of Tables VIII, X, and XI are shown in Figures 3, 4, and 5.

Discussion

The Hydration Capacity of Starches from Different Botanical Sources. It has been long recognized that starches from different botanical sources are not interchangeable in technology, that each starch is especially well suited to some particular industrial use. Table II shows that this property may well be associated with the hydration capacity of the starch micelles.

TABLE VII

THE HYDRATION (AT 30° C.) OF WHEAT STARCH GELATINIZED BY 0.5M NaOH FOR 1 HOUR AT 30° C. (Calculations from the data of Mangels)

		Hard red	spring	Durum		
Conc. of starch	ης	φ	Volume occupied by one gram of starch	η_r	φ	Volume occupied by one gran of starch
P.ct.		P.ct.	Cc.		P.ct.	Cc.
2.0	58.4	61.3	30.65	39.8	57.6	28.8
1.75	34.2	56.0	32.0	27.5	53.67	30.7
1.50	22.3	51.25	34.10	18.0	48.75	32.5
1.25	12.6	44.25	33.2	11.1	42.50	32.0
1.0	7.1	36.0	36.0	6.7	35.12	35.1
0.75	3.7	25.56	34.0	3.9	26.50	35.3
0.50	2.1	15.50	31.0	2.1	15.50	31.0

TABLE VIII

THE HYDRATION OF WHEAT STARCH GELATINIZED IN A 2% SUSPENSION FOR 3 HOURS AT 30° C. BY VARIOUS CONCENTRATIONS OF NaCNS Solutions (Calculations from data of Mangels)

Concentration of NaCNS	η_r	ф	Volume occupied by one gram of starch
Molar		P.ct.	Cc.
1.0	1.1	1.75	0.875
1.2	1.4	7.5	3.75
1.4	1.6	10.25	5.12
1.6	2.0	14.50	7.25
1.8	2.7	20.12	10.06
2.0	4.2	27.75	13.87
2.2	12.2	43.8	21.9
2.4	14.8	46.3	23.15
2.6	16.0	47.3	23.65
2.8	17.9	48.65	24.32
3.0	19.2	49.54	24.77
3.4	26.4	53.2	26.6
3.8	32.0	55.35	27.67
4.2	35.9	56.5	28.25
4.6	28.7	54.15	27.07

The data for wheat starch in Tables II, III, and V permit an interesting comparison. The wheat starch data of Samec et al. were secured on starches gelatinized at 120° C. with viscosities run on 1% sols at 25° C. The volumes occupied by one gram of starch in the gelatinized sols ranged from 18.85 to 11.75 cc. Rask and Alsberg (1924) gelatinized their wheat starches at 90° C. and viscosities were determined at 90° C. The volumes occupied by one gram of starch in their gelatinized sols ranged from 17.47 to 12.51 cc. These data indicate that heat gelatinized wheat starch has approximately the same hydration capacity (volume occupied by one gram) at 90° C. as at 25° C. with the corollary that the decrease in viscosity of the starch pastes at the higher temperature is due almost wholly to the decreased viscosity of the dispersions medium.

TABLE IX

THE HYDRATION (AT 30° C.) OF WHEAT STARCH GELATINIZED BY 1.25M KCNS SOLUTION FOR 6 HOURS AT 30° C. (Calculations from the data of Mangels)

		Hard re	d spring	Durum			
Concentration of starch η_r		Volume occupied by or φ gram of starc				Volume occupied by one gram of starch	
P.ct.		P.ct.	Cc.		P.ct.	Cc.	
5	20.1	50.02	10.0	24.3	52.28	10.4	
4	4.6	29.25	7.3	6.0	33.50	8.4	
3	2.2	16.25	5.4	2.5	18.75	8.4 6.5	
2	1.5	8.75	4.37	1.5	8.75	4.4	
1	1.2	3.5	3.5	1.2	3.5	3.5	

TABLE X

THE HYDRATION OF WHEAT STARCH GELATINIZED IN A 2% SUSPENSION FOR 3 HOURS (AND FOR 24 HOURS) AT 30° C. BY VARIOUS CONCENTRATIONS OF SODIUM SALICYLATE SOLUTIONS (Calculations from the data of Mangels)

Con- centration of sodium salicylate	η _r (3 hrs.)	φ	Volume occupied by one gram of starch	η _r (24 hrs.)	φ	Volume occupied by one gram of starch
Molar		P.ct.	Cc.		P.ct.	Cc.
0.2	1.1	1.75	0.88	1.1	1.75	0.88
0.4	1.1	1.75	0.88	1.1	1.75	0.88
0.6	1.4	7.50	3.75	1.7	11.60	5.80
0.8	2.5	18.75	9.38	3.1	22.50	11.25
1.0	9.4	40.14	20.07	10.2	41.30	20.65
1.4	11.7	43.20	21.60	13.4	45.04	22.52
1.8	17.0	48.00	24.00	21.7	50.95	25.48
2.2	27.5	53.66	26.83	26.8	53.38	26.69
2.4	32.7	55.56	27.78	29.2	54.34	27.17
2.6	35.8	56.50	28.25	_	_	_
2.8	40.9	57.86	28.93	35.0	56.25	28.12
3.0	42.3	58.24	29.12	35.5	56.40	28.20

The Hydration of Heat-gelatinized Wheat Starches from Various Wheat Varieties. Rask and Alsberg (1924) concluded from viscometric data that wheat sorts possessed starches having different physico-chemical properties. A further study of their data, as shown in Table III and Figures 1 and 2, confirms this conclusion, although their data are much more uniform when calculated on the basis of hydration capacity. This is to be expected since it is generally recognized that the viscosity of lyophilic sols is not a direct function of concentration. For example, Rask and Alsberg found a relative viscosity of 267.4 for a 5.86% sol of starch from flour 9528 and a relative viscosity of 595.0 for a 5.57% sol of starch from flour 9297. Rask and Alsberg's data indicate that the starch of flour 9297 differs more than 100% from the starch of

TABLE XI

THE HYDRATION OF WHEAT STARCH GELATINIZED IN A 2% SUSPENSION FOR 3 HOURS AT 30° C. BY VARIOUS CONCENTRATIONS OF UREA SOLUTIONS (Calculations from the data of Mangels)

Concentration of urea	ηr	φ	Volume occupied by one gram of starch
Molar		P.ct.	Cc.
2.5	1.1	1.5	0.75
3.0	1.2	3.5	1.75
4.0	1.4	7.25	3.62
6.0	3.7	25.62	12.81
7.0	8.2	38.12	19.06
8.0	15.8	47.1	23.55
9.0	25.2	52.7	26.35
10.0	29.9	54.6	27.30

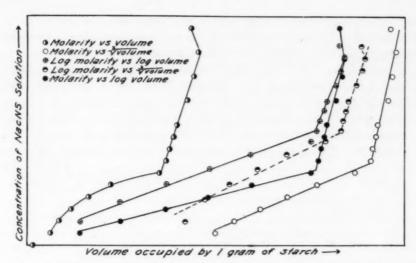


Fig. 3. A graphic representation of various calculations involving the change in volume of the disperse phase in sols of wheat starch during peptization with various concentrations of NaCNS solutions.

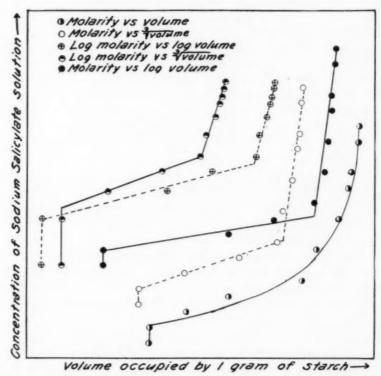


Fig. 4. A graphic representation of various calculations involving the change in volume of the disperse phase in sols of wheat starch during peptization with various concentrations of sodium salicylate solutions.

flour 9528, nevertheless, the degree of hydration appears to differ by only 12% (12.51 cc. and 14.02 cc. per gram respectively). The uniformity of the hydration data is indeed striking.

Figures 1 and 2 show that the volume occupied by one gram of starch decreases with increase in concentration of the starch sol. For some of the starches the decrease in volume is a linear function of concentration, in others a curvelinear relationship exists, indicating that a maximum volume of the starch micelles had been reached in the lower starch concentrations. Rather interestingly, only one of several "French

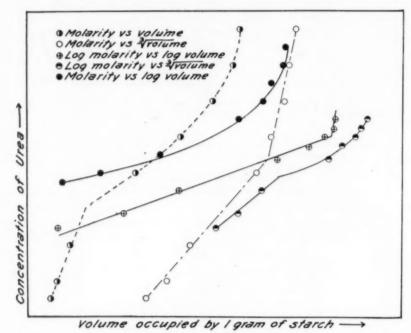


Fig. 5. A graphic representation of various calculations involving the change in volume of the disperse phase in sols of wheat starch during peptization with various concentrations of urea solutions

curves" possessed by the writer fitted all of these volume-concentration curves, indicating that they all followed the same general mathematical formula. Apparently there is competition between the starch micelles for the water available for hydration. This is confirmed by the data for potato starch in Table V.

The Retrogression of Heat-gelatinized Starch. Table IV presents a number of inconsistencies. Apparently a 1% starch sol stored at 58° C. retrogrades much faster than similar sols stored at either 35° C. or 15° C., and also faster than do 2% sols or 4% sols stored at 58° C. However, a 4% sol stored at 35° C. appears to retrograde faster than

similar sols stored at either 15° C. or 58° C. Unfortunately no data are available whereby we can decide whether this is an effect of true retrogression or is due to hydrolysis. Apparently an increase in the concentration of the sols "protects" the micelles against retrogression. An explanation of this may be that some catalyst [H⁺ (?)] is adsorbed on the micelles and thus removed from the sphere of action. More extensive studies are necessary before final conclusions can be drawn.

The Effect of Duration of Heating on the Hydration Capacity of Heat-gelatinized Starch. The data in Tables V and VI show that continued heating of gelatinized starch pastes causes a rapid decrease in the hydration capacity of the starch micelles. Here again the decrease is relatively less rapid for the more concentrated sols, indicating that the micelles "protect" each other against the effect of heat. Table VI shows that the higher the temperature the greater is the loss in hydration capacity. Again the data in Tables V and VI are incomplete since they do not distinguish between effects of hydrolysis (dextrin formation) and simple changes in hydration capacity. The data do show, however, that apparently wheat starch sols are much less affected by prolonged heating than are potato-starch sols.

The Hydration Capacity of Cold-gelatinized Wheat Starches. The data in Tables VII to XI permit some interesting comparisons. In the first place it is evident that the hydration capacity of wheat starch gelatinized in the cold by means of chemicals is of an entirely different order of magnitude than is the hydration of heat-gelatinized sols. Heatgelatinized wheat starch occupies a volume of 12.5 to 17.5 cc. per gram, whereas, when it is cold-gelatinized the volume approximates 28 to 35 cc. per gram. All of the chemicals studied behaved essentially alike in this respect, although the maximum hydration was reached at widely different chemical concentrations. Apparently the maximum hydration is not quite reached by a 3.0 molar solution of sodium salicylate or a 10.0 molar solution of urea whereas it is passed in a 4.6 molar solution of NaCNS. Probably when the chemical solution is more concentrated than that necessary for maximum hydration of the starch we are dealing with an osmotic dehydration where the increased osmotic pressure of the dispersions medium is competing for the water in the hydrated micelles.

A study of Figures 3, 4, and 5 indicates that at least 3 different reactions are involved. At the lower chemical concentrations the starch is not hydrating (cf. Fig. 4). As the concentration of the chemical is increased there is a rapid change in the volume of the starch micelles until again a critical concentration of chemical is reached when a second much slower hydration takes place. This continues until the maximum hydration capacity is attained following which the slow dehydration (cf.

Figs. 3 and 6), which has been suggested as being due to osmotic forces, begins.

It is difficult from a study of the curves in Figures 3, 4, and 5 to determine just what types of reactions are taking place. Apparently the only relationships which fit all three systems are the log molarity vs. log volume and the molarity vs. $\sqrt[3]{volume}$. In each case these yield two widely diverging straight lines. The $\log \times \log$ curves might indicate two different adsorption isotherms, which hypothesis appears, tentatively, as the most promising point of attack. The series of straight line relationship shown in Figures 3 and 4 are exceedingly puzzling—the author knows of no other series of data which shows such similar relationships when plotted with such widely different coordinates.

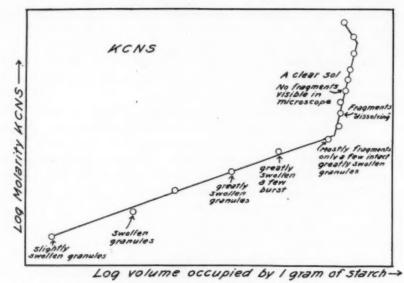


Fig. 6. A graphic representation of the change in volume of wheat starch during peptization with KCNS solutions of various concentrations, including microscopical observations on the appearances of the sols, at various stages of peptization.

Mangels (1932) studied the microscopical appearance of the KCNS-starch systems and Figure 6 drawn from calculations derived from his data, and including his comments on the microscopical appearance, show that the first of the two intersecting straight lines is due to the swelling of the *intact* starch granules and that the second of the intersecting straight lines is due to the *peptization of the smaller micelles* after the granules have burst. The point of intersection of these two lines apparently denotes the "bursting point" of the granules. When the data are plotted with relative viscosity and salt concentration as coordinates, as used by Mangels, this relationship is largely obscured.

General Considerations. It is evident from the above discussion that the Kunitz formula has yielded valuable information when applied to starch viscosity data. It has also indicated many problems for future solution. One of these is the effect of starch micelles upon each other. In some instances reactions are slowed down—in others they are accelerated. The effect of starch concentration in accelerating cold gelatinization (Table IX) requires explanation. It may be that the explanation here lies in the fact that starch absorbs water differentially from the salt solution, leaving a more concentrated solution of potassium thiocyanate behind and this stronger thiocyanate solution then causes an increased swelling of the starch granules. Thus the more concentrated starch suspensions are actually in contact with stronger salt solutions. Unfortunately the data at present available do not permit the testing of this hypothesis.

Summary

The Kunitz formula for converting the relative viscosity of lyophilic sols into a value expressing the volume occupied by the disperse phase has been applied to the viscosity data of starch sols. The following conclusions are evident:

1. Starches derived from various botanical sources differ widely in hydration capacity.

2. Wheat starches from different wheat sorts differ somewhat in hydration capacity, but not nearly so much as the values for the relative viscosity of the respective sols would indicate.

3. The hydration capacity of wheat starch (volume occupied by one gram of the heat-gelatinized starch) is apparently the same at 90° C. as at 25° C.

4. The continued heating of gelatinized starch pastes produces a rapid decrease in the hydration capacity. This change is much more rapid for potato starch sols than for wheat starch sols.

5. Cold gelatinization of starch with chemicals is not the same phenomenon as heat gelatinization. Cold gelatinized wheat starch occupies a volume of 28 to 35 cc. per gram whereas heat-gelatinized wheat starch occupies only approximately one-half this volume.

6. The cold gelatinization of starch by chemical action appears to involve identical reactions irrespective of the chemical which is employed, e.g. NaOH, NaCNS, KCNS, sodium salicylate or urea, although the maximum hydration of the starch occurs at widely different concentrations of the chemical.

7. Cold gelatinization of starch involves at least 3 different reactions. (1). At low chemical concentration no hydration takes place. (2) As the concentration is increased a rapid swelling of the intact granules oc-

curs, resulting eventually in a rupture of the granules. (3) The individual micelles released from the starch granules continue to increase in volume (peptization) through an increasing concentration of the gelatinizing chemical. (4) Finally, as more chemical is added, the concentration of the chemical in the dispersions medium becomes so great that a slow osmotic dehydration of the hydrated micelles takes place.

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THE INFLUENCE OF THE COMPOSITION OF YELLOW CORN ON THE EFFECTIVENESS OF A RACHITOGENIC RATION

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Experimental rickets are usually produced by feeding recently weaned Albino rats either the McCollum, Simmonds, Shipley, and Park (1921) or Steenbock and Black (1925) rations. The Steenbock rachitic ration, consisting of 76% yellow corn meal, 20% wheat gluten, 3% calcium carbonate, and 1% sodium chloride has been used regularly in this laboratory. It was assumed, as is apparently the case in other laboratories, that the components of the ration when purchased in the open market were sufficiently uniform as regards protein, vitamins, ash. calcium, and phosphorus content so that the nutritive value of the ration was fairly constant from lot to lot. Obviously in assaying various products for vitamin D it is essential that a comparable degree of rickets shall be produced in experimental animals. Consequently samples of rachitogenic rations, prepared under uniform routine methods and representing about one hundred pounds of ration, have been routinely analyzed for moisture, ash, calcium, and phosphporus content. The results of these analyses are reported in Table I which also includes the computed ratios of calcium to phosphorus.

TABLE I
RESULTS OF ANALYSES OF RACHITOGENIC RATIONS

Diet number	Ash 3	Calcium 1	Phosphorus 1	Ca/P ratio
	P.ct.	P.ct.	P.ct.	
1	4.23	1.149	0.270	4.259
2	4.95	1.434	0.276	5.198
3	4.29	1.253	0.308	4.062
4	4.28	1.308	0.286	4.578
5	3.77	1.224	0.288	4.253
6	3.93	1.205	0.282	4.273
7	4.13	1.353	0.317	4.264

1 Reported on dry basis.

² Parts calcium to one part of phosphorus.

It will be noted in Table I that the ash content varied from 3.77% to 4.95%, the calcium from 1.205% to 1.434%, the phosphorus from

0.270% to 0.317%, and the calcium-phosphorus ratio varied from 4.062 to 5.198 parts of calcium to one part of phosphorus. Four of the seven rations, Nos. 1, 5, 6, and 7, had nearly the same ratio of calcium to phosphorus. These data raised a question as to the composition of rachitogenic rations prepared in other laboratories. Accordingly, samples of rachitogenic rations were obtained from other laboratories for examination and the results of the analyses are reported in Table II.

TABLE II
RESULTS OF ANALYSES OF RACHITOGENIC RATIONS

Diet number	Ash 1	Calcium 1	Phosphorus 1	Ca/P ratio ²
	P.ct.	P.ct.	P.ct.	
8	3.48	1.265	0.145	8.724
9	2.03	0.656	0.147	4,465
10	3.85	1.506	0.288	5.231
11	2.77	1.154	0.153	7.529

1 Reported on dry basis.

The ash content of the four rations under consideration varied from 2.03% to 3.85%, the calcium from 0.656% to 1.506%, the phosphorus from 0.145% to 0.288%, and the calcium-phosphorus ratio varied from 4.465 to 8.724 parts of calcium to one part of phosphorus. In comparing these results with those obtained in this laboratory it will be noted that the calcium-phosphorus ratio for sample No. 9 is in close agreement with sample No. 4 but the ash, calcium, and phosphorus content of the latter sample is twice that of sample No. 9. Obviously, the calcium-phosphorus ratios of 7.529 and 8.724 parts of calcium to one part of phosphorus are in no sense in agreement with the calcium-phosphorus ratios obtained for the rachitogenic rations manufactured in this laboratory. In view of these wide divergencies it seemed highly desirable to study some of the factors which influence the effectiveness of the rachitogenic ration.

Since ground yellow corn comprised the major portion of the ration and since, presumably, it would show greater variation in composition than the other ingredients of the ration, attention was first directed to it. In this connection it may be noted that McCollum, Simmonds, Becker, and Shipley (1925) have reported their inability to produce experimental rickets in Albino rats when hard instead of soft wheat was used in the preparation of the ration recommended by them. Samples of ground yellow corn were procured through the courtesy of milling concerns.¹

² Parts calcium to one part of phosphorus.

¹ The samples of ground yellow corn discussed in this paper were supplied by Frank E. Boling, Ralston Purina Company; O. B. Kent, The Quaker Oats Company; and A. G. Philips, Allied Mills, Inc.

In requesting the samples it was specified that the ground corn should be prepared from yellow corn and should contain the entire kernel, but no provision was made concerning which milling process should be employed in grinding the corn. To obtain data concerning the possible influence of locality on mineral composition the samples were secured from various corn-producing centers. When the samples arrived they were so different in appearance that it seemed desirable to determine the degree of fineness to which the corn had been ground. The amounts that passed through various sieves are reported in Table III.

TABLE III
FINENESS OF GROUND YELLOW CORN (WHOLE KERNEL)

Labora-	Meal passing through designated sieves							
tory number	No. 70	No. 60	No. 50	No. 40	No. 30	No. 20	No. 12	Refuse
	P.ct.	P.ct.	P.ct.	P.ct.	P.ct.	P.ct.	P.ct.	P.ct.
12	54.2	60.4	73.9	82.0	95.7	99.3	99.9	0.1
13	36.1	45.4	53.7	60.2	74.9	91.2	100.0	0.0
14	46.8	60.3	72.6	80.0	92.6	99.0	100.0	0.0
15	56.7	61.2	71.1	77.4	88.4	98.6	100.0	0.0
16	41.7	51.3	60.5	68.5	84.4	98.0	100.0	0.0
17	55.0	59.3	68.6	75.1	86.5	96.4	100.0	0.0
18	54.7	59.2	70.1	79.0	90.9	99.6	100.0	0.0
19	58.4	62.5	73.7	76.7	87.8	95.4	99.6	0.4
20	23.8	28.1	35.8	41.9	55.5	75.3	100.0	0.0
21	43.6	48.3	56.2	61.7	73.3	86.4	99.4	0.6
22	13.0	14.7	17.7	20.7	27.3	40.0	87.2	12.8

It is very evident from Table III that different milling procedures were employed in grinding the different lots of corn represented by the samples under consideration. More than four times as much of sample No. 19 passed through a No. 70 sieve as of sample No. 22. In fact no two samples of corn were ground to the same degree of fineness. The radical difference in the fineness and texture of samples No. 19 and No. 22 is indicated by the accompanying microphotographs.

It will be noted that sample No. 19 is both finer and more uniform than sample No. 22. Inspection of the particles of corn indicated that sample No. 19 was ground by the "attrition" process and sample No. 22 by the "roller" process. It is evident from these data that, whenever possible, laboratories should purchase whole corn and mill it under carefully controlled conditions. However, many laboratories are not equipped with necessary milling machinery, and hence must purchase corn meals on the open market.

It is obvious from the above data that rachitogenic rations prepared from ground corn of such a variation in fineness will not be identical. Even though the rachitogenic rations might be homogeneous mixtures



Fig. 1. Microphotographs of corn-meal samples Nos. 19 (left) and 22 (right).

when first prepared, subsequent handling would cause separation of the different sized corn particles, as well as the other components of the ration. Data concerning the fineness of the other constituents of the ration—gluten, calcium carbonate, and salt—are reported in Table IV.

TABLE IV
RESULTS OF DETERMINATION OF FINENESS OF CONSTITUENTS OF RATION

	Percentage of ration passing through designated sieves						
Constituent	No. 100	No. 70	No. 60	No. 50	No. 40	No. 30	No. 20
	P.ct.	P.ct.	P.ct.	P.ct.	P.ct.	P.ct.	P.ct.
Gluten	51.6	80.3	87.5	94.1	96.1	99.5	100
CaCO ₃	100	100	100	100	100	100	100
NaC1	0.1	12.7	20.3	53.3	73.0	95.3	100

It is apparent from these data that whenever the ration was handled the calcium carbonate would tend to sift to the bottom of the container. In fact, the coarser the corn the greater the separation, for the wheat gluten, the calcium carbonate, and the finer portions of the corn would tend to work to the bottom of the container and the larger particles of the corn would rise to the surface. Also laboratory animals frequently develop a habit of pawing their food and thus force the finer portions of a grain mixture to the bottom of the feed dish. Hence, a rat eating from the surface of the ration would obtain a different amount of calcium and proportion of calcium to phosphorus than would be provided by the uniform mixture of the ingredients. Two factors contribute to this change of ratio of calcium to phosphorus, (a) the calcium carbonate which is included in the ration to increase the ratio of calcium to phosphorus sifts to the bottom of the dish leaving the coarser particles of corn at the surface, and (b) the ratio of calcium to phosphorus in the coarser particles of corn which are from the exterior of the kernel is different from that of the finer particles. Forbes, Beegle, and Mensching (1913) report that whole corn (dry basis) contains 0.014% calcium and 0.303% phosphorus, while corn bran (dry basis) contains 0.030% calcium and 0.156% phosphorus, or the ratio of calcium to phosphorus in their sample of corn was 0.46: 1.00, while in the corn bran it was 0.19: 1.00. In a study of the phosphorus content of different parts of the corn kernel Voegtlin and Myers (1918) found that in the same run of corn (Maryland roller mill) the phosphorus content (dry basis) was 0.349% for the whole kernel and 0.301% for the bran. This condition may in a measure account for the variation in the amount of time required to produce experimental rickets in different laboratories or in different groups of animals in the same laboratory.

Goldblatt (1931) has already suggested that the irregularity of de-

velopment of rickets may be due to "the settling out of the calcium carbonate of the diet so that, as consumed by the animal, it does not have the high ratio of calcium to phosphorus which is a necessary condition for the production of rickets by this diet." To remedy this situation he recommends incorporating the constituents of the ration in a solid jelly, which may be produced by cooking the gelatin present in the ration.

In preparing the different samples of ground corn for analysis, care was taken to thoroughly mix them before making determinations of the moisture, ash, calcium, and phosphorus content. Moisture, ash, and phosphorus determinations were made by the methods of the A. O. A. C. (1925), while the calcium determination was made according to that given by Norris, Nelson, and Palmer (1931). The values that were obtained are reported in Table V.

TABLE V
RESULTS OF ANALYSES OF CORN

Sample number	Source '	Ash 1	Calcium 1	Phosphorus 1	Ca/P ratio
		P.ct.	P.ct.	P.ct.	
12	Omaha, Nebr.	2.12	0.221	0.294	0.750
13	Peoria, Ill.	1.62	0.026	0.300	0.087
14 15	Ft. Wayne, Ind.	1.40	0.029	0.249	0.117
15	Buffalo, N. Y.	1.39	0.023	0.268	0.085
16	Denver, Colo.	1.63	0.027	0.342	0.079
17	Ft. Worth, Tex.	1.63	0.032	0.325	0.098
18	St. Louis, Mo.	1.38	0.031	0.252	0.123
19	Cedar Rapids, Iowa	1.35	0.024	0.265	0.091
20	St. Joseph, Mo.	1.53	0.020	0.336	0.060
21	Memphis, Tenn.	1.62	0.022	0.341	0.065
22	Akron, Ohio	1.36	0.018	0.295	0.061

¹ Reported on dry basis.

The water content of the 11 samples varied from 10.25% to 12.45%, the ash varied from 1.35% to 2.12%, calcium from 0.018% to 0.221%, phosphorus from 0.249% to 0.342%, and the ratio of calcium to phosphorus varied from 0.060 to 0.750 parts calcium to one part of phosphorus. It will be noted that the ash content of 2.12% and the calcium content of 0.221% for sample No. 12 is appreciably higher than that of any other sample. In reply to an inquiry concerning the origin of this sample of corn, the firm supplying it stated: "The Omaha corn came from Missouri and was grown on what is known as the Missouriloess type of soil. This is on both sides of the Missouri River in what is known as windblown soil. It is good alfalfa land and well supplied with calcium." While the ash and calcium content of this sample are unusually high its phosphorus content, 0.294%, is less than that of six

² Parts of calcium to one part of phosphorus.

other samples. The ash, calcium, and phosphorus content of no two samples were alike and as a consequence the calcium-phosphorus ratio varies materially for the samples of corn from various parts of the country.

A consideration of the mineral composition of the samples of corn under discussion naturally raises a question as to the relation of these results to those of other investigators. The early investigators reported the calcium and phosphorus content of corn ash, but did not report the amount of ash obtained from the corn which they studied. However, the ratio of calcium to phosphorus in the corn ash should be equivalent to that of the corn kernel. Accordingly the results reported by the early investigators are summarized in Table VI.

TABLE VI

CALCIUM AND PHOSPHORUS CONTENT OF CORN ASH REPORTED BY EARLY
INVESTIGATORS

Date 1	Investigator	Location	Calcium	Phosphorus ²	Ca/P ratio
			P.ct.	P.ct.	
1804	De Saussure	France		83.50	
1844	Letellier	Germany	0.929	21.89	0.042
1848	Salisbury	New York	0.107 - 0.322	21.53-22.25	
1856	Liebig and Kopp	Germany	2.188	19.44	0.113
1859	Stepf	Germany	4.52	19.64	0.230
1860	Von Bibra	Germany	0.500 - 8.08		
1865	Way and Ogsten	Germany	0.407	23.46	0.017
1865	Von Bibra	Germany	1.83-2.26	20.74-21.53	
1871	Von Wolff	Germany	1.55		
1880	Von Wolff	Germany	1.57	19.91	0.079
1891	Scovell and Peter	Kentucky		21.19-23.19	
1898	Wiley	U. S. A.	2.27	15.4	0.148
1898	Wiley	Argentine	1.924	16.010	0.120
1898	Wiley	Bulgaria	2.790	19.94	0.140
1898	Wiley	N. S. Wales	2.340	19.45	0.120

¹ Date of investigation as well as citation to literature.

The calcium content of corn ash varied from 0.107%, reported by Salisbury, for corn presumably grown in New York, to 4.52%, reported by Stepf, for German corn. The phosphorus content of corn ash varied from 15.4%, reported by Wiley, for American corn, to 23.46%, reported by Way and Ogsten, for German corn. The variation in the calcium-phosphorus ratio was from 0.017:1.00, for the corn ash studied by Way and Ogsten, to 0.230:1.00, for the ash reported by Stepf. As noted above, although these calcium-phosphorus ratios are computed upon corn ash they should be applicable to the corn kernels studied by the various investigators noted.

² Computed as total phosphates.

³ Parts of calcium to one part of phosphorus.

In later studies the results obtained for the mineral content of corn have been reported on the "as purchased" basis which has been assumed to mean the total corn kernel. A summary of such studies is reported in Table VII.

TABLE VII

CALCIUM AND PHOSPHORUS CONTENT OF CORN REPORTED BY RECENT INVESTIGATORS

Date 1	Investigator	Moisture '	Ash ²	Calcium ²	Phosphorus ²	Ca/P ratio 3
		P.ct.	P.ct.	P.ct.	P.ct.	
1909	Forbes	13.30	1.28	0.020	0.255	0.078
1909	Forbes	12.08	1.38	0.010	0.300	0.033
1909(a)	Forbes	15.87	1.45		0.235	
1909(a)		16.68	1.36	0.009	0.295	0.031
1910	Sherman et al.			0.006	0.200	0.030
1914	Forbes et al.	10.50	1.26	0.013	0.271	0.048
1914	Forbes et al.	11.31	1.25	0.013	0.269	0.048
1914	Hart et al.			0.019	0.272	0.070
1916	Forbes et al.	10.73	1.28	0.014	0.270	0.052
1917	Forbes et al.	13.45	1.36	0.014	0.279	0.050
1917	Forbes et al.	12.87	1.32	0.011	0.272	0.040
1917	Harris et al.			0.011-0.012	0.389 - 0.415	
1918	Forbes et al.	13.81	1.22	0.009	0.245	0.037
1929	Greaves et al.		1.65 - 1.79	0.130 - 0.180	0.320 - 0.350	0.454
1931	Fraps (Iowa Park)		1.38	0.014	0.271	0.052
1931	Fraps (Beeville)		1.14	0.014	0.210	0.067
1931	Fraps (Nacogdoches)	1.05	0.021	0.214	0.098
1931	Fraps (Troup)		1.37	0.021	0.306	0.069
1931	Fraps (Denton)		1.48	0.021	0.319	0.066
1931	Fraps (Beaumont)		1.18	0.021	0.262	0.080
1931	Fraps (Angleton)		1.16	0.014	0.253	0.055

¹ Date of investigation as well as citation to literature.

2 As purchased basis.

Referring to Table VII it will be noted that the ash content of the different samples of corn varied from 1.05%, reported by Fraps for corn at Nacogdoches, Texas, to 1.79%, reported by Greaves and Hirst for corn grown in Utah. The calcium content varied from 0.006%, reported by Sherman, Mettler, and Sinclair, to 0.180%, reported by Greaves and Hirst. The phosphorus content varied from 0.200%, reported by Sherman and co-workers, to 0.415%, reported by Harris and Pittman. The ratio of calcium to phosphorus varied from 0.030:1.00 for corn studied by Sherman and associates, to 0.454:1.00 for corn studied by Greaves and Hirst. The significance of these variations becomes evident if one computes the calcium-phosphorus ratio of the rachitogenic rations which might have been prepared from these samples of corn. If the corn containing 0.210% phosphorus, grown at Beeville, Texas, had been used in the preparation of a ration, the calcium-phosphorus ratio would have been 7.607:1.00. On the other hand, if the

⁸ Parts of calcium to one part of phosphorus.

corn containing 0.415% phosphorus, studied by Harris, had been used in the preparation of a ration, the calcium-phosphorus ratio would have been 3.836:1.00. After considering these data one is not surprised at the reports which have come from a number of laboratories concerning the occasional impossibility of producing experimental rickets in rats restricted to the rachitogenic ration under discussion.

In attempting to explain the cause of the differences in the mineral content of the various samples of corn discussed in Tables V, VI, and VII, one would naturally consider such factors as the different soils on which the corns were grown and the fertilizers used for their nutrition. Numerous investigators have shown that soils deficient in some essential element have far reaching effects on plants and even on animals consuming the plants. Du Toit (1929), in an article entitled "The Value of Phosphorus in the Cattle Industry in South Africa," cites Du Toit and Bisschop, Easterfield Rigg, Askew and Bruce, Eckles, Becker and Palmer, Evans, Guthrie, Henry, Jensen and Ramsay, Hart and Guilbert, Henry, Huffman and Taylor, König and Karst, Malan, Green and Du Toit, Murphy, Orr, Price, Schmidt, Scott, Theiler and Green, Theiler, Green and Du Toit, Tuff, Welch and others as having studied the nature of phosphorus deficient soils, the nutritive quality of grasses and plants grown on such soils, and the profound physiological changes which occur in domestic animals subsisting on phosphorus deficient forage. These authors report that cattle and sheep pastured continuously on phosphorus deficient soils exhibit stunted growth, delayed sexual development, inhibition of oestrum, reduced milk flow, low reproduction, osteophagia (even to the extent of consuming carcass debris), osteoporosis, fractures, osteomalacia, rickets, and death, depending upon the extent and duration of phosphorus-deficient feeding.

The amount of water or rainfall is also an important factor. Harris and Pittman (1917) have reported that corn grown on identical soils and receiving the same fertilizer, 15 tons of manure per acre, but receiving different amounts of water showed a variation in phosphorus content from 0.393%, when there was no irrigation, to 0.454%, when 30 inches of water was applied. Fraps (1931) correlated the amount of rainfall and the protein content of corn grown in Texas. At Nacogdoches in 1926 the rainfall was 36.2 inches and the corn contained 8.3% protein; in 1927 there was 33.1 inches rainfall and 8.1% protein; in 1928, 26.6 inches rainfall and 12.2% protein; and in 1929, 33.1 inches rainfall and 8.2% protein. He concludes: "The correlation of protein with rainfall was, $0.576 \pm .072$, which is a significant relation."

In an extended study of factors influencing the composition of corn, Evvard and Wallace ² found that samples of yellow corn grown on the

² Personal communication, J. J. Evvard and H. A. Wallace, Des Moines, Iowa.

same farm (near Des Moines, Iowa) and thus having the same soil, fertilizer, water, and climatic conditions varied materially in calcium and protein content. Their data are reproduced in Table VIII.

TABLE VIII
CALCIUM AND PROTEIN CONTENT OF CORN GROWN UNDER IDENTICAL CONDITIONS

Corn number	Calcium	Protein
	P.ct.	P.ct.
1	0.06	8.70
2	0.07	10.60
3	0.07	8.20
4	0.07	11.60
5	0.06	9.90

In commenting upon these results the investigators say:

"The corn which was highest in protein was composed one-half of an in-bred yellow strain known as Baker 164, one-fourth of an in-bred yellow strain known as I-14, and one-fourth of an in-bred yellow strain known as L2428. This corn analyzed over 11% protein. The corn which was lowest in protein and which analyzed slightly over 8% was one-half of an in-bred known as Baker 164, one-fourth of an in-bred known as I-14, and one-fourth of an in-bred known as Mc-Corkindale. The only difference between these two, therefore, was that one contained one-fourth McCorkindale while the other contained one-fourth L2428.

"The ears produced by the cross containing L2428 are generally just a little larger and a little later although the difference is not very great. We have just discovered that the in-bred McCorkindale withstands better than almost any other in-bred a deficiency of phosphorus in the soil. We are quite sure that the in-bred L2428 does not withstand a deficiency of phosphorus so very well although this has not been proved so conclusively as the McCorkindale information."

Unfortunately information concerning the phosphorus content of these five different varieties of yellow corn grown on the same soil is not available. Consequently it is impossible to determine the ratio of calcium to phosphorus present in these corns.

Since corn No. 4 contained approximately 41% more protein than corn No. 3, it is of interest to speculate on the possible effect of such a variation of protein intake on the rate of growth of rats during a vitamin D test. A survey of the literature revealed that more extensive studies in this connection have been made with the domestic fowl than with Albino rats. Ackerson and his coworkers (1926, 1928, 1930) and Mussehl and Ackerson (1931) in their carefully controlled experiments and numerous tests under practical commercial conditions have shown that the rate of growth of young chicks and the yield of eggs from adult birds can be very markably influenced by the protein content of the ration fed. In studying the effect on growth of various protein levels of dry skim-milk in a chick mash, St. John, Carver, Helphrey, Miller, and Cassel (1930) found that by increasing dry skim-milk from 8% to 20% they obtained 30% increase in the rate of growth of their chicks. By increasing the protein content of their experimental ration from 12.87%

to 20.23%, Norris and Heuser (1930) increased the rate of growth of S. C. White Leghorn chicks approximately 25%. Swift, Black, Voris, and Funk (1931) found in a study of the optimum protein content of rations for growing chicks that chicks which received 21.67% (average) of protein weighed, when fourteen weeks old, more than twice as much as others which received the same ration adjusted to a 12.48% (average) protein level.

In an investigation of the nutritive value of lactalbumin, Osborne and Mendel (1924) fed two groups of rats rations identical except that one contained 9% and the other 20% lactalbumin. At the end of the test the animals which received 9% lactalbumin were only about two-thirds as large as those which received 20% lactalbumin. Subsequently these investigators (1926) studied the relation of the rate of growth to diet and compared rations of different protein content. They concluded: "Though the differences are not very pronounced (21 per cent or more as compared with 20 per cent or less) it will be seen that the best records have been made for the most part by the animals on the higher protein intakes."

These data concerning a correlation between protein levels and rate of growth are of interest in connection with the report of Bills, Honeywell, Wirick, and Nussmeier (1931), Hess (1929), and others, that a relation exists between rate of growth and intensity of rickets. However, the validity of this belief has been questioned by Bacharach, All-chorne, and Hazley (1931), and Coward and Cambden (1929).

Klein and McCollum (1931) recently reported that it is possible to produce or prevent dental caries in the Albino rat by controlling the phosphorus and calcium intake. They found that rations containing 0.3424% of calcium and 0.4802% or less of phosphorus induced dental caries, whereas rations containing 0.4012% or less of calcium and 0.5282% or more of phosphorus produced rats immune to dental caries. The ratio of calcium to phosphorus in these two rations is 0.7130: 1.00 for the ration which produces caries, and 0.7595: 1.00 for the ration which confers immunity to dental caries-a difference of only 0.0465 parts of calcium to one part of phosphorus. If this slight variation in the ratio of calcium to phosphorus in an experimental ration represents the difference between the production of and immunity to dental caries, it is interesting to speculate concerning the difference in the skeletal tissue of (a) laboratory animals receiving calcium-phosphorus ratio of 3.836: 1.00 and those receiving a ratio of 7.607: 1.00 as could have been the case for rachitogenic rations prepared from corn studied by other investigators (Table VII); of (b) animals receiving a calcium-phosphorus ratio of 4.465: 1.00 and those receiving a ratio of 8.724: 1.00 (rachitogenic rations No. 9 and No. 8, Table II); or of (c) animals

receiving a calcium-phosphorus ratio of 4.062:1.00 and those receiving a ratio of 5.198:1.00 (rachitogenic rations No. 3 and No. 2, Table I).

In the rachitogenic ration under discussion, vitamin A, which is essential for growth of the experimental animals, is derived solely from the corn. Studies of the vitamin A content of corn have been conducted by Steenbock and Boutwell (1920), Wenholz (1922), Harrow and Krasnow (1922), Jansen and Donath (1924), Steenbock and Coward (1927), and Karshan, Krasnow, and Harrow (1927) who found, in general, that the vitamin A content of yellow corn was variable but decidedly greater than that of the white corn which was shown to contain little or no vitamin A. On the other hand, Blackshaw (1923) maintains that yellow maize is not rich in vitamin A and Bacharach, Allchorne, and Hazley (1931) have questioned whether the Steenbock ration may at times be "deficient in the growth-promoting properties associated with vitamin A."

Hauge and Trost (1928) determined the vitamin A content of cross-bred strains of yellow and white corn which were developed because of their high productivity. They found "that vitamin A was present only in the kernels possessing yellow endosperm and was lacking in the kernels of pure white endosperm, even though they were grown on the same ears." By crossing Surcropper (white) and Ferguson's Yellow Dent (yellow) corn, Mangelsdorf and Fraps (1931) obtained four types, "white, pale yellow, dilute yellow, and deep yellow" all of which may occur on the same ear. They found the vitamin A content of these types to be 0.05 units, 2.50 units, 5.00 units, and 7.00 units per gram, respectively. Russell (1930) conducted a study to determine quantitatively the amount of vitamin A in a white capped yellow dent corn with that of a yellow dent corn (both of which produce yellow meal). He found the yellow variety "to be about 50% more potent with reference to vitamin A than a white capped variety."

In a test at the Indiana Station (Purdue University, Agricultural Experiment Station, 1927) of the vitamin A content of corn with pure white endosperm, with pure yellow endosperm, and corn having white plant characters but a yellow endosperm it was found that the vitamin A content bore a definite relation to the yellow endosperm. Later tests (Purdue University, Agricultural Experiment Station, 1929) of yellow corn and a hybrid corn (one-third yellow) showed their vitamin A content was proportional to the amount of yellow pigment present.

Millhouse, Koser, Rocke, and Hetler (1927) separated the different parts of the yellow corn kernel by hand dissection. They found vitamin A concentrated in the endosperm. They obtained normal growth and protection against lung and eye infections in rats when 5% to 10% of gluten, or 10% to 20% of gluten feed, or whole corn constituted the

sole source of vitamin A. Hetler and Meyer (1928) confirmed these findings and concluded that yellow corn, corn gluten, and yellow corn meal are among the cheapest sources of vitamin A for human food. Meyer and Hetler (1929) determined the distribution of vitamin A in corn-milling products and found that 0.25 gm. of gluten, as a supplement to their experimental ration, was sufficient to cure ophthalmia and produce normal growth.

A study of yellow corn at the Texas Experiment Station (1929) showed a variation of from three to six vitamin A units per gram. Smith (1930) in a study of the comparative nutritive value of yellow corn and the grain sorghums found that one gram of the yellow corn under consideration contained approximately three vitamin A units. Fraps (1931) recently published the results of an exhaustive study of the vitamin A content of corn grown at various locations in Texas under different soil and fertilizer conditions. Analyses of 18 varieties of yellow corn showed a variation of from 5.0 to 7.7 vitamin A units per gram of corn. One variety of yellow corn, Ferguson Yellow Dent, grown during 1928, at 11 different locations contained from 4.0 to 7.1 vitamin A units per gram of corn. This variety of corn grown at the 11 stations for a three-year period showed a variation of from 2.5 to 7.1 vitamin A units per gram of corn. Its vitamin A content was not the same for two consecutive years at any of the 11 stations.

In some laboratories it is customary to prepare an amount of the rachitogenic ration sufficient for a considerable period. According to Kick and Bethke (1929) this is a safe practice in so far as deterioration of vitamin A is concerned for they found little deterioration of the vitamin A content of yellow corn either whole, cracked, or finely ground during storage for one year. On the other hand, Fraps and Treichler (1933) report 60%, 60%, 80%, and 85% decrease in the vitamin A content of four samples of yellow corn stored for from six to thirty months, but they found no significant difference in the rate of vitamin A decrease of ground and whole corn during storage.

Summary

Analyses of samples of rachitogenic rations obtained from different laboratories and consisting of 76% yellow corn, 20% wheat gluten, 3% calcium carbonate, and 1% salt, showed variation in ash, calcium, and phosphorus content, and material variation in the calcium-phosphorus ratio.

Since many laboratories are dependent upon the open market for ground corn, samples were obtained from representative milling concerns. These samples varied materially in fineness, ash, calcium, and phosphorus content, and in calcium-phosphorus ratio.

Several investigators have reported significant variation in the protein content of yellow corn due apparently to the variety of corn and the amount of rainfall.

The literature supplies conclusive evidence that the vitamin A content of yellow corn varies over wide limits probably due to the variety of corn studied and to the conditions under which it is grown and stored.

Calcium, phosphorus, protein, and vitamin A are essential factors in a rachitogenic ration. Any significant change in the amount of the factors influences the effectiveness of the rachitogenic ration. Evidence is submitted which shows that the calcium, phosphorus, protein, and vitamin A content of yellow corn is quite variable. Since the rachitogenic ration in question contains 76% of yellow corn, it is quite apparent that, in order to obtain a uniform degree of rickets in successive groups of experimental animals, attention should be given to the composition of the yellow corn used in the preparation of the rachitogenic ration.

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A DISCUSSION OF THE MEANING OF SOME TERMS USED IN CEREAL CHEMISTRY

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Introduction

While cereal chemists have fairly definite concepts regarding the action of doughs, they differ in the use of the terms used to describe them. Thus Weaver (1928) voiced a complaint, common to all, when he said, "I find it rather hard right here to express myself as I would like to do. A well known member of this Association recently remarked to me that what is most needed by this Association is a vocabulary, so that different members, when in discussion, would not seemingly be in disagreement when as a matter of fact they were in agreement." Price (1927) also states that "it was almost impossible for the baker to tell the flour salesman the kind of flour he desired . . . , owing to the varied nomenclature used in the description of the flour . . . , (the flour buyer) had him so confused that it was almost impossible for him, in the bakers' language, to describe just what he wanted."

The International Institute of Intellectual Cooperation (Anonymous, 1932) has been asked to examine the problem of the coordination of scientific terminology. Various international organizations have undertaken, each in its respective sphere, the compilation of scientific vocabularies. The different branches of science, however, constantly employ, and very often with a different meaning, terms which are common to all of them. It, therefore, appeared indispensable that the coordination of these terms should be undertaken. The International Unions of the Sciences of Physics, Chemistry, and Biology are represented on a committee which recently met for this purpose. Bingham (1930) has given the rheologists an excellent vocabulary and defined many terms, some of which apply directly to cereal chemistry.

At the Twelfth Annual Convention of the A. A. C. C., in 1926, considerable discussion of the terms quality, strength, and stability occurred, and it was decided to leave the definitions for these terms to the baking committee. It is hoped that the present discussion may be of assistance. A survey of the literature revealed a number of fairly well defined concepts, but terms covering a variety of related ideas were used in describ-

ing them. In the following definitions the attempt has been made to select the most common usage of the term proposed to describe any one concept. They are designed only to stimulate critical thought, not to be accepted without question. Many of our ideas are still in a nebulous state, and can be clarified only by more experimental work.

Fermentation Relationships

Cereal chemists are, in general, quite familiar with the major factors concerned in leavening and those often classified under diastatic phenomena, hence this discussion will be limited. Cook and Mallock (1930), as well as others, have shown that above a certain minimum yeast concentration the fermentation rate is a linear function of the amount of yeast. The two factors in autolytic saccharogenesis, viz., enzyme activity and starch susceptibility, have been clearly differentiated by Alsberg (1927), Markley and Bailey (1931), Mangels (1926a), Rumsey (1922), and others. It is probable that the initial activity observed in the Rumsey method (the tangent to the curve at the initial value (Fig. 1), is due to the presence of a small amount of highly susceptible starch or injured starch granules, and thus not much different from the Lintner value. After one hour, however, the susceptibility of the native starch is the determining factor. The Rumsey value measures the increase in sugars during the first hour when both factors are operating, and hence, the sugar level of a non-yeast dough at any instant after one hour should theoretically be equal to the sum of the sugar added in the formula, that present initially in the dry flour, the Rumsey value, and the product of the limiting diastatic activity, as here defined, by the time after one hour (Fig. 1). It is thus apparent that no single diastatic or saccharogenic value will give more than an approximate picture of the sugar level, i.e., of the fermentation potentialities of any flour. The potential sugar level in the yeast dough at any instant after one hour is diminished by the product of the fermentation rate by the time. Calculations of the sugar level from these constants at the moment when the dough enters the proof should be accurate to 0.2%-0.5% sugar for short fermentations. Greater accuracy will necessitate consideration of the initial lag period of the fermentation and the effect of pH change on the activity. The Lintner value in this system becomes of importance only when flour improvers of cooked starch are used. Additions of diastatic malt extract or sprouted wheat simply change the values of the constants, as shown by Collatz and Racke (1925).

In view of the work of Bailey and collaborators, Blish, Swanson, Jørgensen, and many others, it is believed unnecessary to call attention to the fundamental difference between saccharogenic properties and col-

loidal properties of the dough. Nevertheless a few pertinent quotations may help to emphasize this point. Fisher and Halton (1929) state "... so far as the gassing power of a flour is under the control of the miller and baker, it should be regarded as a separate problem from strength." Swanson (1928) also points out that "environmental factors under the control of the baker should not be confused with flour

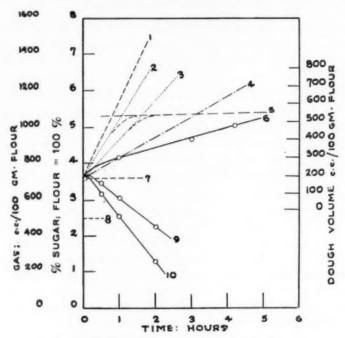


Fig. 1. Fermentation Relationships in Doughs.

- 1. Lintner diastatic (Saccharogenic) activity.
- Fermentation rate with 2% yeast.
 Fermentation rate with 1% yeast.
- 4. Rumsey diastatic (Saccharogenic) activity.
- 5. Maximum dough volume.
- Sugar level in a non-yeast dough. (Data of Collatz and Racke, 1925.) The slope of the straight portion of this curve is termed the Limiting Diastatic (Saccharogenic) activity in this discussion.
- 7. Intial sugar level (sugar content of the flour).
- 8. Sugar added in formula.
- 9. Sugar level with 1% yeast.
- 10. Sugar level with 2% yeast.

quality," while Blish and Hughes (1932) state, "those test loaf properties that reflect the character of the gas retaining agency, i.e., the gluten, have diagnostic value only when there is definite assurance that there has been an adequately maintained gas production." Jørgensen (1931) states positively that, " . . . care must be taken . . . that the volume of the finished test loaf will be a function of the 'strength' of the flour only and not a function of the 'strength' as well as of the 'gassing power' (diastatic activity)." In the succeeding discussion of response and bread characteristics it will be understood that saccharogenesis and sugar levels have been completely eliminated as a factor.

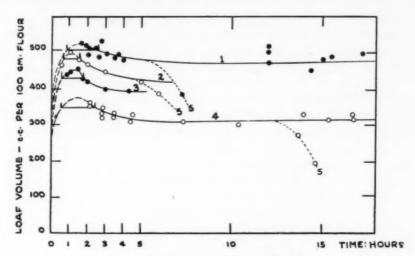


Fig. 2. Fermentation Response and Tolerance.

- 1. Davis and Cline (1926); 300-gram loaf (?); Missouri Soft flour.

- 1. Dayls and Cliffe (1920); 500-gram loaf; Low grade flour.
 2. Clark (1929); 100-gram loaf; Low grade flour.
 3. Grewe (1928); 100-gram loaf; Kansas Hard patent flour.
 4. Swanson and Kroeker (1932); 100-gram loaf; Kansas Hard flour.
 5. Dotted curves showing the drastic effect on loaf volume of low sugar level. The heavy horizontal lines marking off the peaks of the curves are arbitrarily drawn between what might be considered the limits of acceptable texture and illustrate the concept of fermentation tolerance as the effect on the inherent properties of the dough, and not the effect of the environmental factor, sugar shortage.

RESPONSE: Development, Tolerance, Resistance

The nomenclature in this division of the field is not so clearly outlined, as is to be expected from the greater complexity of the gluten system. From many statements by Swanson (1928, 1930), Blish (1928), Working (1928) and others, it may be concluded that response means the showing "of some effect in return to a force" or condition; to answer (Webster's new International Dictionary). Thus, development is positive response, tolerance is neutral response, and, although not so well distinguished, resistance 1 is negative response. Swanson (1930) found that some flours give a "positive response," some a "negative response" and some "no response" to mixing. Herman and Hart (1927) like "to think and speak of flour characteristics in terms of positive, neutral, and negative reaction." Merritt, Blish, and Sandstedt (1932) ask the question: "To what extent do flours actually vary

¹ This term, although used in an inverted sense in this connection, occurs generally in the ature: e.g., ¹⁶ poor resistance" to bromate. Suggested alternatives are regression, degradation, literature: e.g., weakness, depression.

in their response to some of the numerous 'differential treatments' or 'supplementary procedures' that may conceivably be used in flour testing?" As will be developed later, response may be measured as a difference in loaf volume at constant or comparable textures.

It is generally agreed that the system under consideration is one of many dimensions, mathematically speaking, and seldom can more than two or three of these dimensions be clearly comprehended at once. In the process of making dough, *time* is the most important dimension to be considered. It is obvious that the dough may vary in response to varying values of imposed force (mixing, bromate, salt, etc.), when impressed upon the system at different times. In a three dimensional diagram, Fig. 3, time may be plotted along the conventional X axis, re-

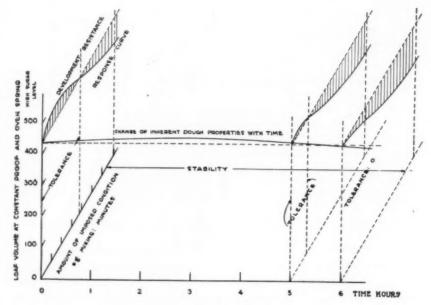


Fig. 3. Illustrating Response.

Development, tolerance, and resistance or negative response. Fermentation constant at \pm 3.2 grams sugar fermented.

sponse vertically along the Y axis, and amount of imposed force or condition (e.g., bromate) along the conventional minus Z axis. Then the response curves, as ordinarily given, will appear in the response-force plane. If another force is simultaneously applied to the system, e.g., mixing, there is a fourth dimension to consider, and the best that can be done at present is to confine our observations to one of the infinite number of three dimensional systems occurring in the complex, i.e., to a constant value of the additional force, or forces. Thus, if mixing response is studied, the amount of fermentation should be constant,

and if bromate response is under consideration, the amount of fermentation and mixing, including that occurring during the raising of the dough, should remain constant. Blish (1927) speaking of analytical tests in general expressed this idea in his discussion of the experimental baking tests: "A given test is carried out in precisely the same way for every sample of the material under consideration. A specified test, performed on a given sample of material, should always present the same picture, whether repeated by one or by different individuals. The most important consideration is that the only *variable* is the material to be tested." May this be amended to read, "The most important consideration is that the only variable is *one of the factors*, and *one only*, as far as our knowledge and technique permit, of the flour or dough complex."

This terminology involves one important departure from that in common use in the literature. The terms bromate response, bromate tolerance, mixing response, and mixing tolerance, are commonly accepted in the sense as presented here. However, fermentation response and fermentation tolerance have been sadly confused with diastatic deficiency, so-called, or low sugar level, as the term is used in this discussion. The reaction of the dough and dough colloids to the amount of yeast fermentation, as expressed, not necessarily by time but by amount of sugar fermented or gas produced is a well defined concept, whether due to change in pH, fermentation products, or other as yet unrecognized causes. Hence, if consistence in nomenclature is to be maintained, fermentation tolerance should represent the amount of fermentation which a dough can withstand, referring to colloidal properties only, before the volume drops to the initial value, i.e., to that value at which an arbitrary standard loaf of acceptable bread first appears (within that range during which a positive response is obtained), and not the time required to exhaust the sugar, or rather, reduce the sugar level to serious values. Since no method is at present known to raise the dough without the use of yeast (at pH 5.0-5.5) this initial value of the loaf volume is a theoretical one, but as time passes and research methods become more refined this value may be approached. In any event, the existence of this hypothetical concept in no way detracts from the use of the term fermentation tolerance in this manner—the numerical values may simply be less accurate than the other tolerances or responses. Moreover, a certain degree of mixing response is usually present in all doughs, so that the conventional fermentation tolerance curve at high sugar level (Fig. 2) is more or less affected by this mixing factor.²

Finally it should be recognized that each of these responses may be found upon closer investigation to be a resultant of several others. Our

² The mechanical action occurring during the raising of the dough is included in the term mixing.

object is to explain dough behavior from the chemical and physical structure of the flour or dough components. While very little is known of the chemical and physical nature we are beginning to differentiate some of the factors of dough behavior. It is hoped that this presentation of terms may aid in the better understanding of the phenomena by minimizing purposeless argument and discussion.

Strength, Stability, and Quality

These three terms have been the occasion of much heated discussion among cereal chemists. Apparently they are somewhat interchangeably used to express three definite concepts: (1) The quality of the best loaf that can be produced, as measured by loaf volume at constant texture; (2) the range of dough or handling time over which that quality is essentially maintained; and (3) a weighed average of these two characteristics, with or without the inclusion of other flour properties. In a discussion, each person vigorously maintains his own conception of the term, usually resulting in the apparent disagreement so aptly referred to by Weaver (1928).

In spite of many statements to the contrary, we are forced to the inference that the following definitions will probably coincide with a bare majority of the opinions expressed:

Strength: Volume of the loaf produced at maximum fermentation response.

Stability: Range of time in hours over which positive fermentation response is obtained, i.e., period of dough time over which fermentation tolerance remains finite.

Quality: A weighed combination of these and perhaps other factors of the flour complex. There is much to recommend Swanson's (1925) statement that "quality is a relative term and cannot be discussed without some reference to the intended use of the wheat" (and flour). We would rather say that quality is a conglomerate of all the characteristics of the flour, and its desirability for different uses may vary with changes in only one of these factors. For example, Skovholt and Bailey (1931) state: "The single figure score used was partly based upon the method of Larmour (1929) although only loaf volumes, grain, and texture scores were included as factors, since these were considered to be the primary measures of baking strength." Mangels and Sanderson (1925) state that, "the loaf volume obtained by controlled baking is usually considered a good index of baking strength," and later Mangels (1926) writes: "A significant positive correlation was found between protein content and baking strength (as measured by loaf volume) . . ." It must also be inferred from the discussion of Larmour and collaborators that loaf volume, as modified by variations in texture scores, is a direct measure of strength.

However, still later Mangels and Stoa (1931) cast doubt upon former statements: "Large loaf volume and high baking strength were, a few years ago, considered synonomous terms. Recent investigations, however, have to a considerable degree shaken our confidence in loaf volume as final index of baking quality." Kent-Jones (1928), of course, maintains that "loaf volume is not . . . a reliable guide for strength, especially with tin loaves," and recognizes that "so many factors, more or less under the control of the baker, enter into the matter." Blish (1927) states: "Some technicians . . . seek maximum expansion as an indication of 'strength'," and makes his position very clear (1926) as follows: "... the term 'baking quality' refers to the inherent possibilities of a given flour, whereas 'strength' should mean quality together with the ability more or less successfully to withstand a certain amount of variation in handling. Thus a certain soft wheat flour may have excellent quality, that is, it will produce a pleasing and palatable loaf, providing it is carefully and properly handled, but it may at the same time be a 'weak' flour, incapable of giving good results when subjected to mechanical punishment. . . . Thus a flour may have quality without strength, but not strength without quality."

Again Haas (1927) states: "A flour which produces bold, voluminous test loaves on both the long and short fermentation indicates strength and good stability." Earlier in the same paper he states, "Hard wheat flours may be classified as weak, moderate, strong, and very strong. A weak flour will give satisfactory results under ideal conditions if the flour is carefully handled. Strong and very strong flours will give satisfactory results not only under ideal conditions but under various degrees of abuse." It is difficult to reconcile such diverse opinions as have been quoted here.

BREAD CHARACTERISTICS: Loaf Volume, Grain, and Texture

One other topic appears worthy of discussion. It is well recognized that loaf volume, cell size or grain and cell wall thickness are intimately related. Investigators who report loaf volume only as an index of their results usually have taken precautions to maintain texture as nearly constant as possible.

From theoretical considerations of the structure of the loaf it can readily be shown that these factors are related as follows, neglecting the contribution of the film material itself to the volume:

$$V^2 = \frac{1}{n} \left(\frac{w}{3td} \right)^3 = \frac{1}{n} \left(\frac{S}{3} \right)^3$$
, that is $S^3 = 1.4n V^2$.

Where V is the volume of the loaf in cubic centimeters, n the number of cells in the loaf, w the weight of film forming substance, S the area

in square centimeters or the total film of the loaf, t the average thickness of the cell walls, and d the density of the film forming material. If L be the average 3 lineal dimension of one cell this expression becomes:

$$V = \left(\frac{w}{3d}\right) \frac{L}{t}.$$

In baking, certain limitations are arbitrarily placed on n, the number of cells, and t, the thickness of the film, in order that the resulting texture will be acceptable or satisfactory. We then find that as the amount of fermentation is increased the loaf volume increases to a maximum and/or the wall thickness decreases to a minimum. Any or all of these quantities are, at present, an unknown function of the amount of fermention, but their extreme values fix the point from which, according to the majority of ideas expressed in the literature, flour strength should be determined. They are statistical values, and would require many determinations if measured individually. Nevertheless, they are of importance in the establishment of a final standard of flour strength. Mohs (1924) and Ḥarrel (1929) have described practical methods of determining and recording internal characteristics.

In discussing saccharogenic properties it was indicated that environmental characteristics should, in so far as experimental technique permits, be distinguished from inherent properties. As pointed out by Swanson and Working (1926), in their discussion of the theory of the action of colloids in the dough, texture, i.e., the relative values of n, t, and L, are largely influenced by the environmental conditions of dough handling. "It is well known that the manner of working the dough, especially the last time before panning, has a marked influence on bread texture." The extensive studies of Herman and Hart (1927) have emphasized the sensitiveness of the system to variations in technique. Further scientific study of this problem would be well worthwhile.

DEFINITIONS

Of necessity a great deal must be left to inference, for to present all the statements bearing on each term would require far too much space. In some cases of confusion several pertinent quotations will be given.

Definitions Related to Fermentation (Fig. 1)4

Lintner Diastatic (Saccharogenic) Activity: Rate of formation of sugar expressed as grams of maltose per hour per 100 grams of flour

 $^{^{2}}$ Platt has suggested that the shape of the curve showing the distribution of values of L is of as much significance as the mean value itself.

⁴ Since no standard temperature has been adopted, and shop conditions vary, it is suggested that the temperature at which any specific value is reported should be given.

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when acting (preferably in the dough) on an excess of gelatinized starch, soluble starch, or fully ground starch. In the determination of Rumsey diastatic activity the tangent to the curve at zero time is very nearly the diastatic activity as here defined. Alsberg (1927) after a critical review of the literature states: "The assumption, very generally made, that the diastatic activity of a flour is always and necessarily an expression of its diastase content is untenable."

Rumsey Diastatic (Saccharogenic) Activity: Rate of formation of sugars, preferably expressed as grams of sugar per hour per 100 grams of flour of standard (13.5%) moisture content when acting autolytically on the starch of the flour under consideration, and limited to the first hour of measurement. It is the slope of the secant drawn from the sugar level at zero time to the sugar level at one hour (Fig. 1). It is a complex of the Lintner value and the limiting saccharogenic value. Karacsonyi and Bailey (1930) state: "This suggests that the Rumsey method for measuring diastatic activity may fail at times to afford an adequate basis for estimating the fermentation potentialities of a wheat flour. . . ."

Limiting (Saccharogenic) Activity: Rate of sugar formation 6 expressed as grams of sugar per hour per 100 grams of flour acting autolytically on the starch of the flour and taken after the first hour of autolysis. It probably represents the enzymic activity of the flour when acting on raw starch of a susceptibility equivalent to that of the starch of the flour under consideration.

Fermentation Rate: Rate of disappearance of sugar expressed as grams per hour per 100 grams of flour (dough containing 100 grams of flour) or rate of appearance of gas, expressed as cc. per hour per 100 grams of flour. The stoichiometrical relationship between the sugar and gas is about 210 cc./g. for bakers' yeast (Schultz and Kirby, 1932) under normal salt concentrations.

Sugar Level: The concentration of sugars in a yeast dough at any time, expressed as grams of sugar per 100 grams of flour.

Potential Sugar Level: ⁷ The concentration of sugars in a theoretical non-yeast dough at any time, expressed as grams of sugar per 100 grams of flour.

⁵ Note the possibility of correction for inversion of sucrose by molds or yeast in the flour in the analytical determination of this quantity by reduction methods.

⁶ As indicated by Landis (1933) the rate of formation of sugars in a fermenting dough is a complex function, consisting of a linear and a logarithmetic phase. It is suggested that the term limiting saccharogenic activity be related to the slope of the logarithmetic phase of this reaction; viz., the "secondary value, s." The slope of the curve is then (s/log 2).

⁷ It has recently been found, and the results can be verified by proper interpretation of others

⁷ It has recently been found, and the results can be verified by proper interpretation of others in the literature, that the diastatic activity in yeast doughs, is often quite different from that in non-yeast doughs made from the same flour. Therefore, it is believed that the following definition more nearly expresses the concept involved:

[&]quot;Potential Sugar Level: The theoretical concentration of sugars in the dough or suspension at any time if the fermentation rate were zero. It is the sum of the concentrations of unfermented and previously fermented sugars at any time."

Dough Volume: The volume of the dough at any time expressed as cubic centimeters per 100 grams of flour.

Maximum Dough Volume: The volume of the dough expressed in cubic centimeters per 100 grams of flour when the rate of loss of gas from the dough becomes equal to the fermentation rate.

Proof (Sugar) Level: The concentration of sugars in the dough at the beginning of proof time expressed as grams of sugar per 100 grams of flour.

Residual (Sugar) Level: The concentration of sugars in the bread after baking expressed as grams of sugar per 100 grams of flour.

Gassing Power: Potential sugar level converted to cubic centimeters of gas per 100 grams of flour, either by the use of excess yeast or the factor 210. While this is not using the term exactly in the sense proposed by Jørgensen (1931), it is believed to be in accord with the other terms suggested in this discussion. Identical with FERMENTA-BILITY (St. John and Hatch, 1931).

Definitions Related to Colloidal Properties

Response: Difference in loaf volume in cubic centimeters per 100 grams of flour ⁸ resulting from the imposition of a definite amount of any condition or substance upon the dough system. POSITIVE response (difference plus) is termed DEVELOPMENT; NEUTRAL response (difference zero) is termed TOLERANCE; NEGATIVE response (difference minus) is termed RESISTANCE.

It is to be understood that this term refers only to the *colloidal properties of the dough*, and is to be regarded as entirely separate from *saccharogenic properties*, as the sugar level, being under the control of the baker, may easily be adequately maintained in the dough.

In order to measure a specific response, every other single condition, as far as experimental technique can be controlled, must be held constant. It is largely because of extraordinary difficulties of this nature that reproducible and highly accurate results are so difficult to obtain, necessitating recourse to variance analysis of a large number of replicates. Thus, in Figure 3, illustrating mixing response in a most general way, we note first the hypothetical curve representing the change of gluten or dough colloidal properties (measured by loaf volume at acceptable texture) with the time in the dough. The plasticity measurements of Sharp and Gortner (1923) and others are probably the closest ap-

⁸ It is realized that this figure will also depend upon the size of the loaf. It is suggested that where this is other than a 100-gram loaf the size of the loaf may also be stated.

⁹ We have taken the liberty of postulating the existence of a standard acceptable loaf (vide supra) *i.e.*, one possessing an arbitrary combination of minimum acceptable characteristics, grain, texture, shred, etc., other than volume. Again it should be emphasized that this at present is a theoretical concept, one which as yet can be but crudely approached in practice, but some reference point for the measurement of response must be provided. More experimental work will probably be required to enable one or more standards to be set.

proach we have to the nature of this curve. Suppose the dough were mixed for varying periods, fermented for two hours with 2% yeast, and baked. Then the response of the flour under consideration is given by the curve in the plane perpendicular to the time axis. Since a constant amount of fermentation equivalent to the conversion of 3.2 grams of sugar has been superimposed upon the system, these particular coordinate axes represent one of an infinite number of such axes which in turn represent the relationships in the system fermentation-mixing-time-response. We have fixed two of these variables, hence we may observe the interdependence of the other two. Again, suppose the dough were given zero mixing (minimum) at the beginning, and then after 7 hours' fermentation was mixed (punched) to varying amounts. A new response curve would be obtained, which, as we well realize in the case of mixing response, shows a greater negative response over an equal range of mixing, or a decreased tolerance.

These concepts may be applied to the action of any other variable of the system. For example, at constant time, say, 2 hours or 4 hours, with mixing constant the response of the dough (measured by loaf volume) to varying amounts of fermentation may be measured. In this case suitable corrections for the resulting variations in fermentation rate during proof time and oven spring must be made, if the true fermentation response is to be obtained.

Bromate Response, Mixing Response, Fermentation Response, Salt Response, Etc.: ¹⁰ Substitute the corresponding term for 'any condition or substance' under response.

Development: 11 Increase in loaf volume in cc. per 100 grams of flour resulting from the imposition of a definite amount of any condition or substance upon the dough system.

Bromate Development, Mixing Development, Fermentation Development, Salt Development, Etc.: Substitute the corresponding term for 'any condition or substance' under development.

Tolerance: Amount of any condition or substance measured from the point at which the loaf of standard texture first appears, which when imposed upon the dough system will produce neutral response. It represents the range over which positive response is obtained.

¹⁰ The reference point from which measurements of the various responses should be made may offer some difficulty. While it might seem desirable to use the point of appearance of the "standard" loaf as the reference, certain experimental difficulties become evident. Fermentation response, for example, is rapidly changing at that point and may make the differentiation of the two responses difficult. Since it is impossible to bake yeast leavened bread without fermentation, it is suggested that, for the present technique, the effect of this factor on other responses may be minimized by always measuring them at maximum fermentation response. In this range such measurements will be least affected by slight differences in fermentation, as the fermentation response itself is changing at a minimum rate.

¹¹ In practical baking the terms development and conditioning are frequently applied somewhat interchangeably to describe changes occurring in the extensible properties of the gluten in the dough. By inference it is suggested that the term CONDITIONING is more suitable for this concept, and that development be reserved for the change occurring in the final loaf volume.

Bromate Tolerance, Mixing Tolerance, Fermentation Tolerance, Salt Tolerance, Etc.: Substitute the corresponding term for 'any condition or substance' under tolerance.

As has been mentioned previously, the term fermentation tolerance has been the subject of considerable discussion and the factor of gassing power has been but recently definitely and clearly distinguished from it. Swanson (1928) has expressed this idea somewhat indirectly as follows: "Fermentation tolerance is taken to mean the time the dough can lay over after it is properly developed and still produce good bread. It does not refer to the total length of the fermentation period, as this may be longer or shorter with equally good flours, 12 and the period would have to be adjusted for the different flours. . . . Another effect of fermentation is the disappearance of sugar. For this reason diastatic activity has been at times considered one of the factors in flour quality. This is of secondary importance. . . ."

On the other hand Blish and Sandstedt (1927) state, "These experiments suggest the idea that fermentation tolerance, or stability, as ordinarily regarded from the production viewpoint, is an item which is associated more closely with the factor of gas production than with that of gas retention," and later Merritt, Blish and Sandstedt (1932) state: "In straight dough baking, using only simple ingredients fermentation tolerance (the time range over which active yeast fermentation may be maintained) is predominantly dependent upon the maintenance of an adequate sugar supply in the dough," while Blish, Sandstedt and Platenius (1929) state: "If it be true that fermentation tolerance depends more upon sustained gas production than upon gluten quality, it follows that variations in fermentation tolerance must be directly proportional to corresponding variations in diastatic power." Moen (1930) also states: "In order to differentiate between flours of varying strength a baking formula must have time and temperature so adjusted that diastatic capacity is severely taxed." The definition of fermentation tolerance herein proposed is in complete harmony with the terms bromate tolerance, mixing tolerance, etc., in common use, and conflicts in no way with the nomenclature of the fermentation industries.

The concept of fermentation tolerance as an inherent flour property, the response of the flour colloids to fermentation, as contrasted with that of a sugar deficiency in the dough, an environmental factor, is illustrated in Figure 2. The heavy horizontal lines giving the fermentation tolerance from the point of view herein advocated, independent of fermentation rates, are, arbitrarily drawn, and depend upon the texture. While it is true that the mixing factor is not quite constant in these results, its effect is probably small compared with that of fermentation.

¹² Our italics.

Haas (1927) recognizes the importance of texture when he says: "A comparison of the texture and grain on the long and short fermentation test loaves gives a valuable indication as to the stability or fermentation tolerance of flour, or in other words, its ability to withstand variations in fermentation." Sharp and Gortner (1923) found that "doughs containing all the ingredients except yeast showed little change in their imbibitional properties on standing," and Dunlap (1926) explains that "the conditioning of gluten in the dough is a function of the H-ion concentration and depends on the phenomenon of gluten dispersion." With respect to sponges Harrell (1926) shows that "it is not the sponge fermentation time that must be watched so closely, but the dough fermentation time. . . . There is no doubt that the straight dough is the best test, as the results are reflected in the dough period of the sponge."

Resistance: Decrease in loaf volume in cubic centimeters per 100 grams of flour or per cent resulting from the imposition of a definite amount of any condition or substance upon the dough system.

Bromate Resistance, Mixing Resistance, Fermentation Resistance, Salt Resistance, Etc.: Substitute the corresponding term for 'any condition or substance' under resistance.

Strength: ¹³ "Ability of a flour to produce large, well piled loaves" (Humphries, 1905), "provided that the gas production factor is sufficient" (Kent-Jones, 1927), "under (scientifically) controlled baking (conditions)" (Mangels and Sanderson, 1925). Measured numerically in cubic centimeters per 100 grams of flour, by the loaf volume at maximum fermentation response with zero (minimum) mixing and with texture constant (practically, texture satisfactory within closest observable limits). This seems to correspond to the general usage of the term, although there are some who differ (vide infra). Harrell (1927) has introduced a specific volume concept into classification of commercial loaves, expressed as cubic inches per ounce: extreme limits; 680 and 520 cc. per 100 grams of flour.¹⁴

¹³ It seems desirable to measure strength at maximum fermentation response because this response is a fundamental characteristic of all yeast raised doughs. It should be noted that the other responses have little bearing on the determination of strength. Thus, although a positive bromate response usually indicates a strong flour, a negative bromate response by no means classifies a flour as weak. Swanson and Kroeker (1932) in reporting collaborative results on baking qualities of flours from four typically strong wheats, using various tests including the bromate differential and mechanical modification, state: "One of these chemists ranked the flours as all strong, several said that the flours could be ranked in different ways depending on the objective." We are inclined to believe that bromate or mixing response should be considered as factors separate from strength, although their bearing on the complex of flour quality may be quite significant.

The question arises as to the relation existing between loaf volume and weight of flour used. That is, what factors influence the choice of relative pan size, proof volume, and amount of dough. Fitz (1924) found variations in the ration of pan volume to dough weight of 1.34 to 4.48 cc./gm. Such variations may explain the marked differences in the absolute values of loaf volume illustrated in Figure 2. As a logical basis for reporting such variations Landis and Freilich (1933) have offered for consideration a concept consisting of the ratio of actual loaf volume to maximum dough volume, expressed as percentage, as determined under identical handling and panning conditions. This has been termed the "characteristic" loaf volume.

Stability: Period of dough time over which tolerance remains finite. It is the time range over which an acceptable loaf may be obtained under any small value of the imposed condition or substance. In Figure 3, for example, the tolerance has decreased nearly to zero at six hours. Hence the mixing stability in this case should be six hours. Stability as ordinarily used in the literature appears to be a combination of fermentation and mixing stability.

It should be recognized that many of these terms represent idealized concepts. This may leave us with no words available to describe some of the phenomena observed under actual conditions, which are frequently a result of the interaction of several of these factors. Where such is the case, it may be desirable to describe the phenomenon by a double term, e.g., mixing-fermentation, or process tolerance.

Summary

A discussion of the published views of many investigators on the process of bread production shows it to be readily divisible into two general fields: (1) Fermentation relationships and environmental factors, and (2) inherent flour properties and colloidal factors. Definitions for several terms used in a variety of senses are proposed with the hope that they may help to clarify the nomenclature of the science.

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VARIATION OF PROTEIN QUALITY IN WHEAT GROWN IN AQUEOUS CULTURE MEDIA

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In another paper, the writer (1933) advanced the thesis that variation in the quality of protein of wheat flour, as expressed by bread scores, is due to certain inorganic elements absorbed in excess of the amount required for the production of the crop in question. That plants may absorb more nutrients than needed for yield obtained is generally inferred from such concepts as "luxury consumption," "the law of diminishing increments of yield with increasing increments of limiting factor applied," and analogous terms appearing in the literature of plant nutrition. But to differentiate the quantities of each nutrient absorbed by wheat—the fraction on which yield was dependent from that on which it was not—necessitated a technique by which nutrients could be withheld from the culture medium during the latter growth periods of the plants so as to preclude absorption. The water culture method of crop production permitted such treatment.

Method Used to Control Plant Growth

The method of production of wheat in aqueous culture media on a scale sufficiently large to provide samples for milling and baking operations consisted, in essence, of a seedbed mounted over and in contact with a water surface which was provided by long shallow reservoirs filled with water. The seedbed consisted of poultry netting stretched tightly over the tops of the reservoirs, and burlap resting on the wire to hold the seed sown broadcast thereon. The seed was covered with sawdust in order to maintain sufficient moisture to effect germination and, upon sprouting, the roots penetrated the burlap and entered the water. Each reservoir, depending on size, contained one or more "fertilizing units." A fertilizing unit, a bottle with restricted outlets, contained the essential elements compacted therein as solid salts. The elements were discharged into the water in such rate, quantity, concentration, and proportion of element to element as was required to maintain the proper physiological condition for growth of plants. The elements required in large amounts were supplied by some of the fertilizers used for land; elements required in small quantities such as boron, manganese, copper, and iron, if not present in the land fertilizers in sufficient quantities, were supplied by other inexpensive salts. The fertilizing units met all the requirements of the plant, so far as the mineral nutrients were concerned, without any further attention. Occasionally, water was added to the tanks, but even this could be avoided, if reservoirs of sufficient depth were used. As the technique for wheat production in water medium on a large scale was, in principle, similar to that worked out for other crops in the development of the method as a practical means of crop production, full description must await publications under appropriate titles.

Purpose of the Method

The purpose of growing wheat in liquid media was to control the quantity of inorganic nutrients absorbed and also to regulate the distribution of the absorption in terms of growth periods of the plants. It was anticipated that by such technique differences could be caused to prevail in the concentration and composition of the sap and in the ash content of the plants, and as a consequence affect the quality of the protein. It was assumed that variations in the quality of protein, as expressed by the baking score, were caused by the character of the sap functioning as a salt solution surrounding the protein molecule or some of its components during certain stages of growth. Differences in the physical properties of protein and starch in wheat flour presumably must result from the vagaries of climate in affecting the supply and distribution of available solutes in the soil. Protein and starch, the chief constituents of flour, need to be considered in bread making in terms of colloidal phenomena. The properties of colloidal particles, as demonstrated in classical experiments, are affected by the nature of the medium surrounding them, and as plant sap is essentially a salt solution varying in concentration and composition, it appeared as not improbable that experiments could be devised showing relations between bread properties and cultural treatments of the plants designed to affect the character of the sap.

The thesis that excess absorption of inorganic elements by the growing plants is the cause of differences in the quality of protein, as expressed by the baking score, would presuppose that the absence of excess absorption would preclude variation in bread arising from this factor. Variation in quality of bread is essentially digression from a standard or type chosen to serve as a basis for comparison. For the nonce, the standard to be considered is a hypothetical loaf baked from flour in which the total quantity of all inorganic elements absorbed by the plants functions causatively in grain production. This hypothetical

standard loaf, as will become apparent in the course of the paper, can easily be obtained, but as it was not a factual accomplishment in this experiment, its physical characters as measurements are not available. In order that elements of nutrient nature may be absorbed in excess of the plant's requirements, it is necessary that conditions be made to prevail which will permit absorption of the elements but will also preclude their utilization as necessary components of total production. Essentially the required condition is absorption during the latter growth stages of the plants, so late that the time subsequent to the absorption of the quantity in question is too brief to permit utilization in terms of new vegetative growth. That is, due to the imminent maturity of the crop, the physiological state of development precludes a renewal of earlier processes, essential to initiate new growth units. A growth unit, in terms of the mineral nutrition of the wheat plant, may be defined as the maximum possible weight of all materials which, at normal maturity of the plant, have become united with and developed from a specific quantity of an inorganic element absorbed during a prior growth period. The sum of the growth units of a plant is, therefore, the total yield of crop at maturity.

It is possible to differentiate the total quantity of any element absorbed by plants into two fractions, one on which yield is dependent, and the other on which it is not dependent. Furthermore, the state of development at which given increments of an element are absorbed, serves as a means of distinguishing two different categories of the nutrients held in plant tissue. First, the nutrients absorbed early are needed for vegetative development. At maturity this portion of the total amount of nutrients absorbed represents the irreducible minimum quantity causatively associated with crop yield. Second, the nutrients absorbed late are not capable of causing new growth, but by their mere presence in the plant modify the final composition and physical character of the crop. The increments of absorption occurring early in growth, and becoming specific organic parts of the mature plant, presumably cannot effect variations in the composition of the final product, because differences in the amount of any one element absorbed, considered in the rôle of a limiting factor, is reflected in variations in the magnitude of yield and not in composition; that is, yield, segregated into increments of growth, is expressed by a straight line function to the absorption of corresponding increments of the nutrient element occurring only during the early growth stage of the plants.

Some qualification to the above should be made as plants vary markedly in the manner in which they segregate their total production into grain (seed), straw, leaves, and roots. As these fractions differ greatly as to chemical composition, and as the relative proportion of

each of these products varies among species, consequently the length of time an element may be precluded from the nutritive medium without impairment of normal development varies both among wheat varieties and plant species generally. Spring wheat can reproduce itself from the nitrogen or phosphorus present in each well filled kernel without any additions of either of these elements from the outside. The grain so produced obviously will weigh less than the original seed, because some of the nitrogen or phosphorus was needed for the production of nongrain tissue and thereby became inaccessible to the grain. Nutritive elements like nitrogen or phosphorus, which can be excluded from the culture medium during the entire growth of the plants without impairment of their reproductive functions, save as to quantity, reveal a straight line function in the relation of increments of the elements absorbed and total yield obtained. But iron, calcium, or potassium belong to another category, for not only does the seed contain insufficient quantity of either of these elements to effect reproduction without additions from the outside but these elements need to be available in the culture medium for a considerable portion of the growth period before either can be withheld from absorption without impairment to reproduction. The straight line relation between increments of yield of normally constituted mature product and those of either of these elements does not apply until after a certain stage of development has been obtained when an additional increment will effect reproduction. Deviation from a straight line expression indicates absorption occurring too late in the growing period of plants to become causatively related to crop yield. Superimposed on that which is absorbed early, it becomes the fraction whose physiological effect cannot be predicated inasmuch as the quantity does not become an organic part of production.

An increment of growth, in terms of an increment of inorganic element absorbed, is essentially the sum of the weights of all materials taken up by plants which enter into organic relation with the quantity in question in such a way that if the specific increment were not absorbed no addition would occur to the weight of the plant. However, increments of any inorganic element may be absorbed without any additions to the weight of the plant save that of its own mass, which, however, is negligible or nearly so. While the absorption of a specific increment of an essential element is growth in a limited sense, nevertheless, it cannot be expressed as growth in the organic sense because it does not result in the agronomic entity "yield of crop." While a very small fraction of the weight of a crop is due to the weight of inorganic elements derived from soil, nevertheless the relation of this fraction to the chief and determinative elements in yield—the combustible materials—is profound and far-reaching. The clue to the largest yield of wheat grain possible

per unit area of space lies in the manipulation of conditions in such a way as to obtain the widest possible ratio between the inorganic and combustible fractions of yield imposed upon the largest possible quantity of inorganic materials plants can be made to absorb. (This will be developed in another paper.)

Withholding all inorganic elements from absorption during the latter growth phases of wheat has the effect of reducing the percentage of ash in the plants to low values, granted the plants continue to grow. As the reciprocal of low ash value is high value for the non-ash constituents of yield, one of the conditions necessary for maximum production of grain is thereby obtained. The large measure of growth secured after the inorganic nutrients are precluded from absorption is further evidence that the gain in weight due to the combustible fractions of a crop is not dependent on the simultaneous absorption of inorganic nutrients. Thus, due to the opposing direction of two distinctive yet dependent processes involved in crop production, there prevails a period in the development of wheat when the concentration of the sap and the amount of inorganic nutrients absorbed are determinative factors of yield, and another period follows the above when the absorption of inorganic elements, no longer needed for the production of the combustible fraction of yield, becomes modifiers of the character of the crop.

It is, therefore, postulated that if there is no excess absorption of inorganic elements, there is no variation in the composition of the organic units of production among yields of different magnitudes. Yield is simply an expression of the number of organic units or growth increments produced, each of which may be considered as conceived in the early growth stage of the plant. The inorganic elements are a factor in their conception, but absorption, subsequent to certain as vet undefined initial growth stages, plays no part in the development of these organic units. It appears reasonable, therefore, to assume that there can be no organic variation in the composition of the various growth increments at maturity, for differences in the amount of inorganic nutrients absorbed during the early growth stage of the plants cause differences in yield and thereby preclude differences in composition. Standardization of wheat varieties in terms of bread quality should proceed from a fixed physiological basis in regard to the nature of the crop. The minimum ash content of the mature wheat plant appears as the logical basis from which to proceed in a study designed to obtain correlation between bread qualities and variation in the nutrition of the plants.

Experimental

For a comparison of the bread qualities of wheat in terms of character or quality of proteins, it is necessary to have samples alike in the

percentage of protein as well as in other properties known to affect baking qualities. Treatments designed to effect differences in the quantities of inorganic nutrients absorbed by simply precluding the absorption during the latter growth stages of some samples and not of others, also effect differences in the percentage of protein in the samples. differences exist in the absorptive capacities of varieties, treatments could be arranged for obtaining samples alike in percentage protein of the grain and unlike in the amount of inorganic elements absorbed. Some data along this line have been secured, but as a more satisfactory method of obtaining experimental material consisted in treatments within single varieties, the results obtained in experiments where variety was a variable will be considered under another title. To obtain samples alike in protein content, but different in ash constituents of the growing crop, an array of cultures were treated as follows: The cultures were treated alike up to the attainment of a growth stage indicated by the emergence of the first visible part of the head. That is, up to this point, the cultures grew in a nutrient medium well supplied with each of the essential inorganic elements required for growth of plants in water. Then each reservoir was drained, the fertilizing units removed, and fresh water supplied. Then, in a series of three reservoirs, the subsequent treatment was as follows: One received Ca(NO3)2, another NaNO₃, and the third KNO₃; each reservoir received two pounds of the respective salt, a quantity in excess of the amount the plants were able to absorb. It was anticipated that the samples would be practically alike as to the protein content of the grain, and unlike in the ash of the vegetative portions of the plant, due both to the quantity and nature of the constituents absorbed. The anticipation proved well founded with Bunyip, but not quite as well with Pusa, as the protein content of the grain in the NaNO₃ set was not equal to that in the Ca(NO₃)₂ or KNO₃ treatments.

The milling and baking operations were carried out according to the directions followed by General Mills in their experimental laboratories. The writer is indebted to C. B. Kress for the use of his laboratories, and for the scoring of the samples as given in Table I.

The cultures of Bunyip treated with different nitrate salts produced grain that was practically alike in percentage protein; likewise also the flour of the several samples varied little in this character. The grain and flour of the culture where nutrients were absent during the latter part of the growth were decidedly lower in protein than samples receiving nitrogen. While some differences in bread quality obtained between representative high protein values and the lower value, nevertheless they need to be considered as being of minor order. Furthermore, the differences in bread quality among the several nitrate treatments when treated

TABLE I EFFECT OF ABSORPTION OF VARIOUS SALTS ON THE BREAD QUALITY OF WHEAT

									Bread score	score		
					Bread	Bread volume	Crust color Crumb color	olor	Crumb	color	Grain and texture	and
Sample	Treatment	Protein in wheat	Protein Protein in in wheat flour	Ash in flour	IsitinI	Stimulated	faitinI	Stimulated	IsitinI	Stimulated	Initial	Stimulated
		P.ct.	P.ct.	P.ct.	Cc.	Cc.						
-	Commission columbia columbia	Variety Bunyip	Bunyip	0,60	25		r		0		c	
77	Complete nurrient solution, entire growin period Complete to first sign of emergence of head; then	13.9	13.0	0.00	610		, ,	1 4	0 0	1 9	A	1 1
3	complete to first sign of emergence of head; then	0,0	0.0	1.0	066	nec	0	n	ю	o	00	n
4	Complete to first sion of emergence of head then	13.4	11.8	0.45	280	585	7	1	10	10	10	6
	solution of NaNOs to maturity	14.2	12.5	0.49	909	460	9	S	10	6	6	S
0	complete to first sign of emergence of nead; then solution of KNOs to maturity	13.4	11.6	0.50	640	555	7	9	10	10	6	oc
		Variety	y Pusa									
10	Same as 1 above	17.3	17.0	0.45	820	740	000	01	10	10	10	01
100	Same as 3 above	18.9	18.	0.52	850	3 18	100	- 1	10	1:	10	. 11
4 rv	Same as 4 above Same as 5 above	15.7	16.3	0.41	845	240	100	10	9	00	00	0

by the normal procedure of the bake shop are also of minor order. However, when the samples were tested by the modified procedure, as expressed by the stimulated loaf, marked differences in quality among the samples occurred. It was evident that the exposure of the cultures to ${\rm NaNO_3}$ for the latter part of the growth period was decidedly injurious to quality as expressed by loaf volume, crust color, and grain and texture of crumb. This evidence is very well illustrated by the photographs of the loaves shown in Figures 1, 2, and 3.

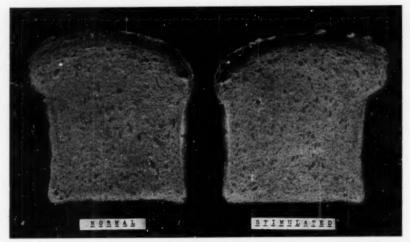


Fig. 1. $Ca(NO_8)_2$ series. Complete nutrient solution to emergence of head then $Ca(NO_8)_2$ solution to maturity. (See Table I, treatment 3, for complete baking data.)

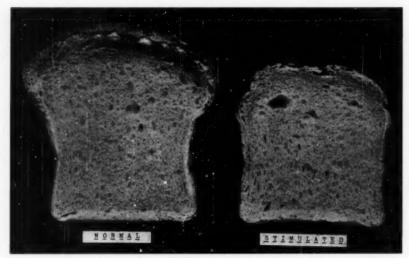


Fig. 2. $NaNO_a$ series. Complete nutrient solution to emergence of head, then solution of $NaNO_a$ to maturity. (See Table I, treatment 4, for complete baking data.)



Fig. 3. KNO_a series. Complete nutrient solution to emergence of head, then KNO_a solution to maturity. (See Table I, treatment 5, for complete baking data.)

The cultures of Pusa treated with different nitrate salts produced grain decidedly higher in protein than obtained with the cultures of Bunyip similarly treated; likewise they differed more among treatments than was the case of the first named variety. The lowest protein value among the cultures receiving nitrate during the latter growth stage was that of NaNO₃. However, as the value was 15.7% it needs to be considered as high protein grain. The results of the baking tests are to be interpreted as being similar to those for Bunyip in one distinctive feature, namely, markedly poorer quality of bread produced from the NaNO₃ treatment. On the whole, Pusa produced better bread than Bunyip, probably, but not necessarily due to higher protein values of the several samples. It is to be noted that greater decreases in loaf volume occurred in the complete, and the KNO₃ treatments than in the corresponding treatment with the NaNO₃ cultures if the stimulated baking procedure is compared with the normal procedure.

Very marked differences were shown in the crust color of the samples of Pusa, as compared with those of Bunyip, the latter being decidedly inferior to the former. Crust color is assumed to reflect diastatic activity, and is related to the amount of sugar in the dough available for caramelization in baking. Bunyip is considered a very good bread wheat under California conditions, and its failure to produce bread of good crust color when grown under glass cannot be explained by any cultural feature, as Pusa was grown under similar conditions. There is a possibility, however, that due to the very dense stand obtained in this variety, insufficient light may have operated to cause the effect noted

and this effect was precluded in Pusa which did not tiller so profusely as Bunyip. An indication of the density of stand of Bunyip is conveyed in the yield of grain which, computed on acre basis, would equal 142 bushels. (Also see Figure 4.) The crust color of the NaNO₃ treatments and of those where nutrients were withheld during the latter growth period was inferior to that of other treatments.

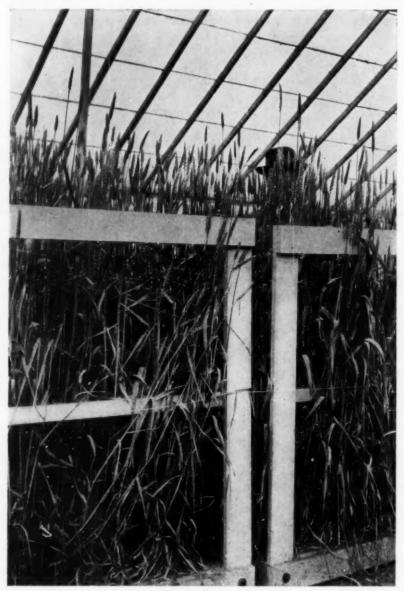


Fig. 4. KNO_a series headed out. (Yield of grain at rate of 88.6 gms. per square foot.)

Until more data have been obtained on the relation between bread quality and cultural treatment of the nature herein indicated, no appraisal can be made as to the mechanics of the processes involved in creating differences in physical properties of the flour. It will be necessary to expose wheat cultures during the latter growth phases to each of the nitrates, chlorides, sulfates, and phosphates, anions of each of the cations, calcium, magnesium, sodium, and potassium, in order to obtain needed data. As the salts absorbed during the early growth stage markedly affected yield, and as certain non-nutritive salts are to be used, it is assumed that, if supplied subsequent to the stage when yield is effected, the plants may absorb relatively large amounts without harmful effect on yield. The flour from the treatments that have yielded marked differences in the quality of bread will later be subjected to analysis, primarily as to physical characters in an endeavor to obtain some light on the colloidal character of both protein and starch in an attempt to explain the laws appertaining thereto. (Experiments are now under way to obtain these samples.)

The water culture method appears to be the only means by which satisfactory material can be obtained for studies on the physical properties of wheat protein as the natural method of culture does not permit investigators to analyze their data in terms of specific and sharply defined nutritional factors. Evidence that inorganic nutrients (nitrogen salts) absorbed during the latter growth stages of the plants may markedly affect quality of the grain, has been provided in the investigations of Moertlbauer (1911), Davidson, and Le Clerc (1917), and Gericke (1920). Milling and baking tests by Davidson and Shollenberger (1926), also by Gericke (1927), have shown that such treatment may reflect itself in bread of greater excellence than that obtained from samples not so treated. But Gericke has also shown that high protein grain obtained by the method described above may result in bread of poorer quality than that obtained from untreated samples and suggested the probability of a process occurring in the latter growth phases of the plants as cause for variation in the quality of the protein of wheat flour.

Wood (1907) appears to be the first investigator who realized the inadequacy of the theory accounting for differences in the strength and quality of bread by differences in chemical composition of the protein, and suggested that differences in the quality of the protein may arise from the salts absorbed by plants. A paragraph of the summary of his paper may be of interest:

[&]quot;The properties of gluten which vary with concentration of acid and salt are coherence, elasticity, and water content, and it is suggested that these properties have an important bearing on the shape of the loaf and knowledge of the acidity and soluble salt content of a flour gives a clue to the factor of strength and decides whether the flour will make a good shaped loaf."

While mechanical features such as the closeness of milling (Dempwolf (1869), Vedrödi (1893), and others) or the length of storage of flour (Bailey and Johnson (1924) and others) affect those factors which Wood named as a clue to strength, nevertheless, their significance needs to be studied in terms of the cultural conditions of the plants rather than by the mechanical means known to affect these characters. In a number of papers, Bailey (1925) has shown how quality in bread is more or less affected by the instrumentation and art employed in milling and baking operations; and has also related various characters of bread to certain chemical entities in flour or dough. Numerous papers in the field bear witness to the complexity of the problem, nevertheless, it appears that a measure of clarification can be obtained by control of the determinative factors of variation in wheat through production of the experimental samples in liquid media.

In the final analysis, diversities of climate, complexities of soil, alteration in cultural conditions, and the peculiarities of varieties are but means to effect differences in the amounts and distribution of elements absorbed by plants in a given space of time. The apportionment of the total quantity of each element absorbed by plants into two fractions, one on which yield is dependent, the other on which it is not, apparently provides the mechanics by which the quality of the wheat grain as expressed in bread is made to vary. Variation can be accounted for; firstly, by changes in composition of the grain, such as differences in the percentage of protein, and secondly, inferentially, by colloidal phenomena expressing themselves in the physical properties of protein and starches. The latter is assumed to be due to the solutes absorbed in excess of the nutritive needs of the plants, and being subject to the vagaries of climate, soils, and culture cause more or less variable salt solutions in the plant which affects the character of colloid particles.

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A NEW CHARACTERIZATION OF THE GLUTEN PROTEINS 1

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(Read at the Convention, June, 1933)

The purpose of this communication is to offer, in a very general way, a revised and possibly a new viewpoint as to the nature of the structural units of which wheat gluten is composed. The conclusions are based upon extensive "fractionation" studies conducted over a period of several years. Details of methods and data, and comprehensive reference to the work of others will be reserved for later publications.

When these studies were first started, it was taken for granted, without question, that gluten is essentially an intimate mixture of two separate and distinct individual proteins, glutenin and gliadin, as designated and characterized by Osborne (1907). Proceeding on this assumption, the purpose was to establish reliable methods for the quantitative separation and estimation of these proteins.

As the work has progressed, innumerable difficulties have been encountered in attempts to prepare and identify "individual" proteins. Results have frequently been irregular, inconsistent, and contradictory. One chief handicap has been the lack of suitable criteria for the evalua-* tion and interpretation of findings.

Protein Dispersing Agents

The first essential in protein fractionation is to find a suitable dispersing agent. The ideal situation would offer a liquid in which all

¹ Published with the approval of the Director as Paper No. 141, Journal Series, Nebraska Agricultural Experiment Station.

the protein material could be completely dispersed, which could then be filtered to remove even the finest particles of undissolved contaminating material without loss of protein, and from which all of the protein could be recovered, either as a whole or in fractions, in its original form and without loss of any of its original properties. No such solvent has yet been discovered for the gluten proteins to the knowledge of the writers.

Several types of dispersing media have been used for the gluten proteins by various workers. These include principally alcohols, alka-

lies, acids, salt solutions, and urea. Each has its advantages.

Alcohol disperses a large portion of the gluten protein; the so-called "gliadin" portion. However, the amount of protein so dispersed, or "extracted," is never definite. It varies with the alcohol concentration, with temperature, with the ratio of solvent to solute, with time, and with the number of extractions. Extraction with alcohol under any given conditions is apparently never complete.

Alkali accomplishes the complete dispersion of all of the gluten protein in a very short time, and these dispersions can be filtered water clear without loss of protein. Unfortunately, however, as has been shown by Blish and Sandstedt (1929), there is always a destructive irreversible alteration of the protein, regardless of the concentration of alkali employed. Most of the protein may be recovered by neutralization of the filtered alkaline extract, but it has lost its original coherence and elasticity. Moreover, it can be shown to have undergone irreversible chemical changes, depending on the concentration of alkali used, or on the time, or the temperature of exposure thereto. These changes are probably hydrolytic in character.

For acid dispersion, acetic acid is given decided preference over other acids. Flour proteins dispersed in dilute acetic acid, alone, seemingly suffer no destructive changes either in chemical or physical properties. When *flour itself* is exposed to dilute acetic acid, the quantity of protein dispersed will vary directly and systematically with the concentration of the acid, other conditions being the same. However, when wet crude gluten is used as a starting point, a dispersion of *all* of the protein is accomplished by acetic acid in almost any concentration.

If a little salt is added to a dispersion of gluten in dilute acetic acid, or if the acid is neutralized, or partially so, the gluten at once coagulates and can be recovered in its original coherent and elastic form. Redispersion and recoagulation can be repeated several times by these methods without noticeably changing the physical properties of the gluten. This situation, in contrast to the destructive alteration by dilute alkali, distinctly favors the use of acetic acid as a dispersing agent.

There are, however, disadvantages pertaining to the use of dilute acetic acid as a dispersing medium for the gluten proteins. Flour, as such, can not be conveniently used for the initial dispersion because, as already mentioned, gluten dispersion is incomplete, the degree of incompleteness varying with the acid concentration. Crude gluten, washed from the flour, must serve as the starting point.

Although these gluten dispersions apparently are and remain of uniform concentration, with no settling out of protein on standing, it appears certain that all of the protein is not dispersed to the same degree. There is obviously a wide range of variation as to size of the ultimate particles. Some of these particles are so large that they clog up the pores of a filter, and render impossible the filtration of the dispersion without loss of protein. Some protein also is thrown out by a Sharples super-centrifuge. Hence, it has not been possible to separate the dispersed gluten protein from contaminating starch, and other material in suspension, by filtration or by the centrifuge. The larger, non-filterable particles are characteristic of the "glutenin" fraction. The "gliadin" portion undoubtedly is more highly dispersed, and filterable, but separation of definite fractions by filtration is not practicable, owing to clogging of the filter due to the gelatinous character of the larger particles.

It is probable that there is a systematic gradation in particle size, depending on the strength of the acetic acid. With high concentrations of acetic acid the "glutenin" fraction becomes correspondingly more "soluble" due either to decreased hydration or diminished aggregation of the ultimate particles. High concentrations of acetic acid, however, present danger of hydrolysis, and in addition to this, excessively large amounts of salt are involved when re-coagulation from concentrated acetic acid is attempted.

Another troublesome feature of dispersions in dilute acetic acid, alone, is the difficulty of obtaining "fractions" by precipitation methods. As stated previously, the addition of small quantities of a neutral salt, or the neutralization of all or a portion of the acetic acid causes practically a *complete* coagulation of the gluten to its original gel form. Larger quantities of certain salts, however, would doubtless bring about a peptization of some of the protein, depending upon the kind and quantity of salt used. This may be predicted from the action of various salts in the peptization studies of Gortner, Hoffman, and Sinclair (1929).

It was considered advisable to obtain protein fractions, if possible, from dispersions in simple pure solvents, and with the avoidance of high concentrations of acids, alkalies, or other electrolytes. Therefore, the more concentrated salt solutions, as used by Gortner, Hoffman, and Sinclair (1929), and reagents such as strong urea solutions, as used by Cook and Alsberg (1931) were excluded in this work.

With the foregoing considerations in mind, and after numerous and

extended trials and experiments with almost every conceivable type of dispersing agent, a definite method for the dispersion of the gluten proteins was finally adopted as best suited for its intended purpose, and the method has been used as a basis for the subsequent fractionation studies. The method involves complete dispersion of freshly prepared, moist crude gluten in dilute (0.1–0.05N) acetic acid, followed by the addition of alcohol to make the final alcoholic concentration approximately 55% by volume.

Protein "Fractions"

Alcohol confers upon gluten dispersions in dilute acetic acid a certain type of stability, which is in distinct contrast to its well-known effect upon emulsoids in general. Let us consider, for example, a gluten dispersion whose acetic acid concentration is 0.05N, and whose concentration of ethyl alcohol is 55% by volume. If no alcohol were present, the addition of a little NaCl, or the neutralization of the acid, or of a portion of it, with NaOH, at room temperature, would produce immediate coagulation of the gluten to its original gel condition. the presence of the ethyl alcohol (50-60%) neither NaCl nor neutralization of the acetic acid cause any coagulation or precipitation at room temperature. If, however, after the addition of a small, definite quantity of NaCl, the temperature of the system is lowered to about 12° C., a fraction of the originally dispersed gluten protein slowly precipitates, leaving a clear supernatant liquid. Further progressive lowering of the temperature accomplishes the progressive precipitation of additional protein "fractions." At minus 12° C. almost all of the gluten protein is precipitated under this set of conditions.

The different protein fractions can, of course, be isolated. They are found to vary, *systematically*, both in physical properties, and in chemical constitution.

With certain variations of procedure similar series of fractions may be obtained, but the necessary temperature adjustments may be entirely different with each set of conditions. A few examples will make this clear.

1. If an exceedingly small amount of $\rm K_2SO_4$ is used in the place of NaCl in the foregoing experiment, the first precipitation occurs at 19° instead of 12° C. Other fractions come down at temperatures correspondingly higher than are necessary in the case of NaCl.

2. If methyl alcohol is used instead of ethyl, no lowering of the temperature is required to precipitate fractions with small quantities of salts. Thus, at *room temperature*, K₂SO₄ will cause the precipitation of a "fraction" that accounts for about 30% to 35% of the entire quantity

of protein. Different salts will precipitate different quantities at room temperature, using methyl alcohol.

3. With methyl alcohol-acetic acid dispersions, neutralization of the acetic acid produces immediate precipitation of a large portion of the protein at room temperature. When ethyl alcohol is substituted for methyl, however, no precipitation occurs at average room temperature upon neutralization, and a slightly lower temperature is necessary to accomplish this.

Thus far there is no established limit as to possible minor variations in the number, quantities and character, respectively, of protein "fractions" that can be isolated from gluten by various modifications of this type of method. Nevertheless, certain trends of properties and behavior indicate that these fractions may be conveniently classified into three main groups.

The three groups may be designated, for convenience, as the "glutenin" group, the "gliadin" group, and a group to which the term "mesonin" has been tentatively and arbitrarily assigned. The name "mesonin" is intended to convey the idea that the protein components of that group have properties which are *intermediate* with respect to the properties of the glutenin and gliadin groups.

It has not yet been possible to distinguish sharp and definite limiting boundaries among the three groups. Indeed, it is not at all certain that distinct boundary limits really exist. Differentiation from one group to another may well be a matter of gradual rather than abrupt change. If the change from one group to the other is actually gradual and imperceptible, then the classification into three groups may be challenged as being arbitrary and unwarranted. Nevertheless, a consideration of certain predominating tendencies indicates that such a classification is convenient and not without justification.

A discussion of comparative "solubilities" will illustrate this point. Alkaline solvents are excluded from the picture, for reasons previously stated. The glutenin portion is but very slightly soluble in alcohol or in *dilute* acetic acid. Starting with flour itself the amount of glutenin that can be dispersed either by alcohol or dilute acetic acid, or a combination of the two, is almost negligible. With moist crude gluten as the starting point, glutenin is *barely* dispersed by dilute acetic acid, but the dispersion is more of a suspension than a solution. It is opaque and unfilterable. Clear, filterable "solutions" of glutenin in acetic acid are obtained only in very high concentrations of the acid. The "glutenin" fraction represents roughly 20% to 25% of the gluten.

The "gliadin fraction" is, of course, predominantly soluble in neu-

² Suggested by C. H. Bailey as an appropriate term to indicate the idea of "intermediate" properties,

tral~50% to 70% alcohol, as well as in dilute acetic acid. These alcoholic dispersions are water clear and filterable. The "gliadin fraction" constitutes roughly 45% to 55% of the gluten.

There remains approximately and very roughly 25% of the gluten unaccounted for. This is the so-called "mesonin" fraction. It appears to be appreciably soluble in neutral alcohol, but not highly so. It is, however, readily dispersed by dilute acetic acid, or by alcohol con-

taining dilute acetic acid, giving a clear, filterable sol.

Thus, in so far as solubilities alone are concerned, there are definite tendencies which suggest the distinguishing of three main protein groups of gluten proteins. The gliadin group is readily soluble both in neutral alcohol (50%–70%) and in dilute acetic acid. The mesonin group is much less soluble in *neutral* alcohol, but highly so in dilute acetic acid. The glutenin group is least soluble in alcohol, and it shows the least dispersion in dilute acetic acid.

That the transitions from one group to the other are not sharp is probably due to overlapping solubilities. If the situation could be graphically shown in the form of a continuous curve, the curve would doubtless show three broad plateaus. Transition from one plateau to another would, however, be represented as a sloping "terrace" rather

than a perpendicular drop with sharp angles.

When gluten protein "fractions" are successively precipitated from acetic acid-alcohol dispersion by progressively lowering the temperature after the addition of salts (or after neutralization), the order in which the three groups are precipitated is what would be expected from a consideration of their comparative solubilities, as just previously discussed. That is, the glutenin group tends to come down most readily and at the higher temperatures, the mesonin group at intermediate temperatures, and the gliadin group at the lower temperatures.

No set of conditions has yet been established which can be said to afford the nearest approach to a quantitative separation of the three groups. In fact, there is no assurance that such a thing is possible. It is probable that each group in itself is made up of "components" varying slightly in properties. Thus, for example, Haugaard and Johnson (1930) have accomplished a fractionation of gliadin preparations merely by lowering the temperatures of alcoholic sols to 0 and minus 11° C. respectively. The fractions showed differences in solubility and in properties such as viscosity and osmotic pressure. That a similar situation is encountered in the glutenin and mesonin groups may reasonably be concluded from the fractionation studies upon which this general report is based.

There are, of course, no known reliable criteria for establishing the number of components within any protein group. Furthermore, little

is definitely known with regard to the nature of forces holding them together. The linkages must be weak in many instances if they can be broken merely by changes in temperature. In such a situation it is obviously impossible to establish specifications for a set of conditions that will insure the complete and quantitative separation of any one of the three main groups of gluten proteins.

It is the present belief of the writers that the gluten proteins may be characterized in a manner which is essentially in conformity with the recently published ideas of Sorensen (1930) as to soluble proteins in general. Sorensen (1930) regards soluble proteins as reversibly dissociable component systems. Each component system is said to consist of a series of "complexes."

"Within each complex all the atoms or atom groups are interlinked by main valencies, whereas the various complexes or components are reversibly interlinked by means of residual valencies. The linkage between the components is comparativly feeble and of such a character that alterations in the composition of the solution (salt-content, hydrogen-ion activity, alcohol content, temperature) can cause reversible dissociations of, and exchange of components between the component systems present. When these alterations in the composition of the solution are so adapted as to render possible the formation in sufficient amount of a component system insoluble or sparingly soluble under the new conditions, this system will be formed and precipitated."

Applying the scheme of Sorensen (1930) to the gluten proteins, the writers would present a picture of three main dissociable component systems, each system in turn consisting of a group of lesser dissociable components or complexes.

Any so-called "purified protein preparations" from wheat flour or gluten probably consists of a group of these dissociable complexes having somewhat similar properties, and preparations having constant properties are obtained only so long as the *same method of preparation* is adhered to in all details. Variations in methods of preparation cause variations as to the components or "complexes" involved, and variations can be shown by measurable differences, both in chemical composition (products of hydrolysis) and in properties such as solubility, coherence, elasticity, viscosity, and susceptibility to denaturation. These differences and variations are *systematic* and *progressive*, as one goes from the glutenin through the mesonin and gliadin groups in the order mentioned.

The only item in which the results of these fractionation studies have seemingly failed to conform to Sorensen's (1930) views has to do with the reversibility of the dissociable component systems. The components or "complexes" of the glutenin system are the most insoluble and the least readily reversible. The gliadin "fractions" are seemingly the most readily reversible and the most soluble. The mesonin group is intermediate as regards both these properties, as would be expected. It

seems highly probable, however, that irreversibility in the glutenin system is due to the fact that in the gel form this system is comparatively readily susceptible to denaturation when in contact with the reagents from which it was precipitated. This denaturation renders it difficult and frequently impossible to re-disperse the system in acetic acid. Neutral reaction favors denaturation. Methyl alcohol has a far greater denaturing effect than ethyl alcohol. Potassium sulfate denatures glutenin protein more readily than do many other salts.

The mesonin and gliadin systems, especially the latter, are less easily denatured, and these dissociable systems are apparently more readily reversible. If denaturation could be completely avoided it might well be found that the entire gluten protein system would conform readily and completely to Sorensen's (1930) viewpoint.

Adequately detailed discussions of methods and data will be presented in later publications.

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AN APPARATUS FOR THE CONVENIENT AND ACCU-RATE DELIVERY OF SOLUTIONS USED IN EXPERIMENTAL BAKING TESTS

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United States Department of Agriculture, Washington, D. C.
(Received for publication June 5, 1933)

Each year the Baking Laboratory of the Bureau of Agricultural Economics, in cooperation with the Office of Cereal Crops and Diseases of the Bureau of Plant Industry, conducts several thousand experimental baking tests. Some of these tests are cake tests but the majority are to determine the bread baking quality of different flours. As this program of work progressed, it became apparent that it would be highly desirable if a device could be developed which would permit more rapid measuring and dispensing of the liquid ingredients of bread doughs or cake batters, and at the same time create conditions whereby errors of measurement could be reduced to a minimum.

Early in 1930 steps were taken to perfect such an apparatus and, as a result of these activities, the equipment which is illustrated in Figure 1 is now presented to the cereal chemistry laboratory personnel as a highly desirable piece of equipment to be used in conjunction with the other precision instruments that are now recommended for use in the A. A. C. C. baking test.

The figure is probably self-explanatory, but it will help to better understand the operation of the apparatus if a description is given of the manner in which the solutions are prepared for making the tests as well as the manner in which a dough or batter is prepared.

Bell jar D contains distilled water, and, depending upon the temperature of the room, it is either preheated by means of a pencil type electric heater, or cooled by means of the refrigeration unit F. The bell jar C contains the yeast solution, which is so made up that each 20 cc. draft furnishes the equivalent of 3 gms. of yeast. The temperature of the yeast suspension is maintained at 50° F. by means of the refrigeration unit F. In order that a uniform suspension can be drawn from the bell jar over a period of $2\frac{1}{2}$ to 3 hours, a variable speed agitator, I, is immersed into the suspension and kept rotating at a speed of approximately 50 r.p.m.

The refrigeration unit consists of a 10 gallon iron water tank which has been heavily insulated with shredded asbestos and encased in copper.

² Grain Division, Bureau of Agricultural Economics.

¹ Office of Cereal Crops and Diseases, Bureau of Plant Industry.

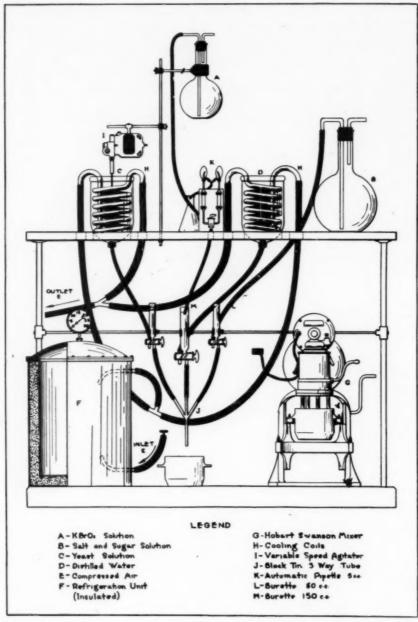


Fig. 1. Appliance for conveniently and accurately dispensing ingredients used in experimental test baking.³

³ Thanks are due to Sidney R. Snider, Junior Chemist, Bureau of Plant Industry, for his painstaking care in preparing the line drawing shown as Figure 1.

Crushed ice mixed with rock salt is placed in the tank, the cover securely clamped down and compressed air allowed to flow from inlet tube E through tubes H to the chromium plated ½ inch copper cooling coils nesting in bell jars C and D and thence out to the waste line through outlet E. Although not shown on the drawing, valves have since been provided to separately control the rate of cold air passing through the coils in bell jars C and D so that the temperature of the contents of each bell jar can be controlled independently of each other. With the yeast solution at 50° F, and the room at 90° F., 20 lbs. of pressure on the gauge will bring the doughs out of the mixer at 86° F.

Flask B contains the combined sugar and salt solution which has been prepared in the proportions called for by the A. A. C. C. formula. A 20 cc. draft of this solution is equivalent to the sugar and salt required in the A. A. C. C. formula. Flask A contains the bromate or other soluble flour improver whose effect one may wish to study.

Assuming the ingredients prepared and in position, a bromated dough would be handled as follows:

The weighed flour is placed in the mixing bowl and this in turn is placed under block tin tube J (glass will suit just as well) and the solutions are delivered through the automatic pipettes M and L in the following order: Yeast, followed by water, then salt. By delivering the yeast solution first, water second, the water will rinse the drippings from tube J, thereby diluting the yeast solution and lessening the danger of the salt and yeast solutions coming in contact. When bromate is used it is measured by the 5 cc. automatic pipette K, and delivered to the water burette M, and is thus introduced into the dough with the distilled water.

When preparing cake batters, practically the same equipment is used. However, an ice bath is used to immerse the mixing bowl of the Hobart mixer. Sometimes, due to extremely high room temperatures, it is also necessary to use the refrigeration unit to maintain the cake batter at a constant temperature. When preparing cake batters, burettes L and M are replaced by burettes of 250 cc. capacity. Bell jar C is used to hold the prepared egg albumen solution. Bell jar D is used to hold the milk-sugar-salt solution. Somewhat different from the shape of the block tin tube as used in the bread dough set-up is the one used in preparing the cake batters. In this case, the tube is "Y" shaped so that it delivers directly to the mixing bowl while the mixing paddles are in operation.

With the equipment described above, it is possible to significantly increase baking capacity with a corresponding increase in accuracy.

The device is simple to arrange, is not expensive, and can be maintained in a sanitary condition with little care.

ADDRESS OF THE PRESIDENT

L. D. WHITING

Ballard & Ballard Company, Louisville, Kentucky

(Read at the Convention June, 1933)

We are now meeting in the nineteenth annual convention of this Association. Another strenuous year has passed, during which time the activities of the Association have been diligently carried on by the various committees. There has been a continuously growing interest in and necessity for the enlargement of committees both in numbers and in personnel. Twenty groups including 70 different members are now engaged in conducting the business and the work of the organization. The progress of many of these activities has been reported periodically through the medium of the News Letter, but at this meeting we shall have the opportunity of learning in detail what has been accomplished during the past year. Final reports will be made this week.

The year has been one of great economic stress through which our membership has not come unscathed. This has been reflected in a net loss in the membership of the Association as of January 1st of four members,—less than one per cent of the total membership. At the same time there has been a small gain in the net assets of the Association. The funds which make up part of the assets are deposited in several banks in different cities. We are pleased to be able to report that all of these banks opened promptly after the bank holiday, and no loss of capital has been sustained.

The Baking Committee typifies the loyalty and cheerful, hard working spirit of every one of the committees. It began its career nine years ago and in that time has made marked progress. Earthquake and storm, fair weather and sunshine have not turned this committee from its purpose. During the past year, under the able leadership of W. F. Geddes, it has carried on in its traditional manner. Inasmuch as the final report of the Research Fellow included several suggestions for further study of a specific character, the committee has undertaken much work on certain specific projects which will be presented as special studies by the individual committee members.

Much can be said of the faithful work of the editorial staff and managing editor of Cereal Chemistry. These men and women have maintained the high standard of our scientific journal in a very commendable manner. Through the cooperation of these individuals, in addition to their regular duties, there has been published and distributed the brochure containing the addresses delivered in 1932 at the presentation of the Osborne Medal to C. H. Bailey.

The publication of the proceedings of the eighteenth annual meeting at Detroit was accomplished during the year and has apparently met with favor. Consequently, the proceedings of this, the nineteenth meeting, will appear in due time. Much valuable information is thus made available to those members who find it impossible to attend the annual meetings.

There are great possibilities for the development of the Association presented in our active sections. The problems to be solved and lines of fruitful investigation to be followed are so numerous that the committees can not begin to attack many of them for some time to come. It is suggested that each section select certain problems in cereal chemistry for collaborative investigation, these projects to be carried on in addition to the check sample work and other work of the section. Two of the sections have already begun studies of problems as above outlined. Such work will increase our knowledge more rapidly; it will encourage greater cooperation among a greater number of chemists, better acquaintanceship, and better methods of analysis.

It is most gratifying to report the splendid cooperation that has existed during the year between the Association of Operative Millers, the American Society of Bakery Engineers, and our own Association. We shall be privileged to join with these two associations in a joint session on Thursday morning. On that occasion, we will hear C. M. Parks, President of the Association of Operative Millers, and C. S. Pickering, President of the American Society of Bakery Engineers. All three of the associations, being engaged in the same great industry of furnishing bread to humanity, have much in common. Each association has its problems which frequently merge with the others, and the solution of which can only be accomplished by teamwork in this vital cause.

I want to express to my fellow officers my appreciation of the excellent spirit of cooperation in which they have responded to all demands on their time during the past year. I desire to thank the chairmen and members of the various committees all of whom have accepted and carried out their duties so cheerfully and efficiently. With this kind of cooperative spirit pervading the organization, the outlook for the future is bright and most encouraging.

I have only one recommendation to make to this assembly, and this may be embodied in the old homely phrase, "Keep on sawing wood."

MINUTES OF THE NINETEENTH ANNUAL CONVENTION OF THE AMERICAN ASSOCIATION OF CEREAL CHEMISTS

M. D. Mize, Secretary-Treasurer

Medinah Athletic Club, Chicago, Illinois

June 5-8, 1933

Monday, June 5

Convention called to order at 9:30 a.m. by President L. D. Whiting.

Invocation by Rowland J. Clark, Chaplain of the American Association of Cereal Chemists.

Dr. Herman S. Bundeson, Director, Health Department, City of Chicago, delivered a message of welcome in which he emphasized the value of cereals in a proper nutritional diet.

President Whiting delivered the address given on pages 370-371 of this issue of CEREAL CHEMISTRY.

The following committees were appointed by President Whiting:

Resolutions Committee: H. G. Walter, Chairman, H. W. Putnam, R. A.

Nominating Committee: L. R. Olsen, Chairman, R. K. Durham, C. E. Mangels.

Auditing Committee: W. L. Heald, Chairman, R. K. Durham, Geo. R. Stadler, R. C. Sherwood, M. J. Blish.

In reverence to the memory of Fred L. Ward and A. W. Meyer, deceased since our 1932 convention, the members assembled stood two minutes in silence.

The chairmen of the local sections present were introduced to the convention. Paul Schulze, of the Paul Schulze Biscuit Company of Chicago, delivered a few words of greeting as a representative of the Chicago Baking Fraternity.

Dr. Paul Pelshenke from the Halle University, Germany, was introduced. Communications of greeting were received and read from the following: R. Mayo Crawford, President, Allied Trades of the Baking Industry; H. A. Lockwood, President, Bakery Equipment Manufacturers Association; Carl Pickering, President, American Society of Bakery Engineers; Henry Stude, President, American Bakers Association.

L. J. Schumaker, Chairman of the Board, American Institute of Baking, delivered an address, "Modern Use and Supply of Cereals."

Music—Big Ten Singers of Chicago.

Dr. Gustav Egloff, Research Director Universal Oil Products Company, Chi-

cago, delivered an address, "Radical Changes in Industry Due to Modern Research."

A motion picture describing some applications of chemistry to baking, taken by Robert Brooks, Manager, Bakeries Research, Standard Brands, was shown through the courtesy of Standard Brands.

C. B. Morison, Chairman of the Convention Program Committee, was introduced and commended for the excellent program scheduled for this convention.

Meeting adjourned at 12:00 noon by President Whiting. Meeting called to order 1:30 p.m. by President Whiting.

Meeting then placed in charge of C. H. Bailey, chairman for the afternoon. Paper by M. P. Neumann, Institut für Backerei, Berlin, read by title. Paper—"Rancidity", by H. O. Triebold.
Paper—"A New Characterization of the Gluten Proteins", by M. J. Blish and

R. M. Sandstedt; read by M. J. Blish.

Paper-"Inorganic Constituents of Wheat and Flour", by Betty Sullivan. Paper-"Some Effects of Heat Exposure on Wheat Starches" Report of Committee on Standardization of Laboratory Baking, W. F. Geddes,

Chairman.

Sub-report—" Scoring Crumb, Grain", by C. H. Bailey and M. C. Markley. Sub-report—" The Wheat Meal Fermentation Time Test", by M. C. Markley and C. H. Bailey.
Sub-report—"Further Experiments with the Short Method in Laboratory Test

Baking", by R. M. Sandstedt and M. J. Blish.

Sub-report—" Notes on the Standard Baking Test as Applied to Whole Wheat

Flour", by R. T. Bohn and F. D. Machon.
Sub-report—" Variability in Loaf Volume Characteristics as Influenced by (1) Dough Mixing Machinery (Hobart-Swanson vs. Hobart Mixer), (2) Dough Mixing Procedure (Mixing 200-gram doughs and dividing (a) after mixing, and (b) after fermentation), (3) Size of Dough (200-gram doughs vs. 100-gram doughs), and (4) Freshness and Brand of Yeast."

"Comparison of Variability Incident to Experimental Milling as Contrasted

to Experimental Baking in the Evaluation of Wheat Strength." By D. A. Cole-

man, C. C. Fifield, P. Talbott, and Ray Weaver.
"Studies on the Working Centrifugal Method for Determining Absorption."

By C. C. Fifield.

Sub-report—"Test with Motor Driven Laboratory Dough Sheeter." "Dia-static Supplements for Experimental Baking." By C. N. Frey, read by J. Freilich

Start Supplements of Experimental Milling in Evaluating Wheat Strength." "The Influence of Experimental Milling in Evaluating Wheat Strength." "Studies of the Hobart Swanson vs. Hobart Mixer." "Studies on Sheeting Rolls." "Low Form vs. Tall Form Baking Tins." "Studies on 100 Gram, 50 Gram and 25 Gram Doughs." By W. F. Geddes, et al. (Studies in Baking Formula: The Effect of Ammonium Phoses.

Sub-report—"Studies in Baking Formulæ: The Effect of Ammonium Phosphate on Loaf Volume", by R. K. Larmour.

"Some Relationships between Sugar, Diastatic Malt, and Potassium Bromate in the Baking Formula", by R. K. Larmour and S. F. Brockington.

"A Comparison of the Blish Short Method with a Number of Other Baking Formulæ", by R. K. Larmour, A. G. O. Whiteside, and W. F. Geddes. Sub-report—"Report on Centrifugal Absorption Method", by E. B. Working.

Meeting adjourned at 5:30 p.m.

Tuesday, June 6

Meeting called to order by President Whiting at 9:00 a.m., and placed in charge of C. G. Harrel, chairman of the morning program, the colloquium of the Local Sections of the Association.

Northwest Section, G. Moen, Chairman, presented, "Century of Progress in Starch Chemistry", by C. H. Bailey, O. Skovholt, L. R. Olsen, and Section Mem-

Niagara-Frontier Section, N. L. Gregory, Chairman, presented, "A Section Meeting—All Wet", by N. L. Gregory, J. H. Julicher, and Section Members. Pacific-Northwest Section—"Submitting Remains."

Midwest Section, L. E. Jackson, Chairman, presented, "Recovery of a Sick Loaf", by W. C. Luckow, W. G. Epstein, G. Rasmussen, J. Micka and I. A. Berg. Nebraska Section—"Crust Characteristics on Pup Loaf an Index of Dough Development", by A. A. Andre.

Pioneer Section, H. W. Putnam, Chairman, presented, "A Mill Laboratory", by C. F. Davis, H. D. Liggitt, R. B. Potts, and H. A. Baehr.

Central States Section, H. G. Walter, Chairman, presented, "Cakes", by V. E.

Fisher, L. G. Brown, C. O. Oppen, and M. B. Graff.

Kansas City Section, C. H. MacIntosh, Chairman, presented, "Characteristic Section Meeting", by Members of Section.

New York Section, Bert D. Ingels, Chairman, presented, "Staling of Bread", by John C. Baker, C. A. Glabau, and Quick Landis.

First prize in the colloquium won by the Northwest Section, second prize by the Midwest Section, and booby prize by the Pioneer Section.

Meeting adjourned at 12:00 noon,

Wednesday, June 7

Meeting called to order by President Whiting at 9:00 a.m. R. L. Frye moved the Minutes of the 1932 convention by M. D. Mize, Secretary-Treasurer, be approved as printed in CEREAL CHEMISTRY, Vol. 9, No. 4, page 438. Seconded, carried.

C. E. Mangels moved the Annual Financial Report of the Secretary-Treasurer for the year 1932 be approved as printed in CEREAL CHEMISTRY, Vol. 10, No. 2, page 167. Seconded carried

page 167. Seconded, carried.

R. K. Durham read and moved that the Auditing Committee Report be approved as printed in Cereal Chemistry, Vol. 10, No. 2, page 169. Seconded,

carried.

Report of Editor-in-Chief

D. A. Coleman

The only comments that the Editor-in-Chief has to make are with regard to material for the journal. Simultaneously with the changed economic conditions, there appears to be a decided shortage of worthwhile technical papers. It is urged, therefore, that those of you who have material in the making, organize it and forward it to us promptly.

C. E. Mangels moved that the report of the Editor-in-Chief be accepted.

Seconded, carried.

Report of the Managing Editor

C. C. Fifield

The report of the Secretary-treasurer published in the May, 1933 issue of Cereal Chemistry includes the financial statement for the journal during the year of 1932.

It is gratifying to report that during the year when other associations were experiencing difficulty in financial matters affecting the size of their journals, that Cereal Chemistry published a larger volume than ever before and still showed a profit. This was made possible only by rigid economy on the part of the editors, a slightly increased general revenue, and a lower page cost per issue.

a slightly increased general revenue, and a lower page cost per issue.

It is interesting to note that the cost per page has been reduced to \$7.54 in 1932 as compared with \$9.18 in 1928 and \$8.76 in 1929, or a saving of \$1.64 and \$1.22 per

page over the years 1928 and 1929, respectively.

Lower printing costs have perhaps accounted in no small measure for a substantial portion of this saving, without, of course, sacrificing the workmanship and affecting the quality of the journal.

Those interested in the other financial aspects of the journal may consult the Secretary-Treasurer's report where such facts are listed, and I believe self-

explanatory.

J. A. Dunn moved that the Report of the Managing Editor be accepted, Seconded, carried.

Report of the Executive Committee

R. C. Sherwood, Chairman

The duties of the Executive Committee during the period between conventions are largely financial, involving the approval of expenditures, the signing of checks by the chairman, and consultation with the Secretary-Treasurer regarding the dis-

position of funds.

The Association's funds are distributed in several banks, all of which opened promptly following the bank holiday, with no loss of our capital. It is the policy of the Committee in the investment of funds to rank security of principal ahead of earning power. The Committee believes that U. S. bonds offer the greatest security for long time investment. Part of our reserve has been so invested and more will be transferred in the near future.

It is the policy of the Committee to live within the income of the Association, adding a small amount to the reserve each year, if possible, in order to protect against emergencies. The time is approaching, however, when the Association should consider using a portion of the income from the invested reserve for some

laudable purpose

During the past year the Committee approved the expenditure of \$301.00 for recording, printing, and mailing the proceedings of the 1932 Convention, a copy of which each member received months ago. This innovation was instituted during R. K. Durham's administration. It is a service to members of the Association

only, not to subscribers to CEREAL CHEMISTRY. This printed report should be particularly valuable to those members who are unable to attend the annual meeting. The plan is being followed this year and the expense has been budgeted by the

Committee

The Committee approved the expense of printing the brochure covering the presentation of the Osborne Medal to Dr. C. H. Bailey. Credit is due C. B. Morison for assembling and arranging the various speeches, and to the editorial staff of Cereal Chemistry for their part in editing, printing, and financing of the brochure. Members should bind both the brochure and convention proceedings with Cereal Chemistry for a permanent record.

As usual, the Executive Committee was active in determining policies regarding the annual meeting. The Committee strongly favored restricting the meeting to four days. It is realized that a full program is the result, but the prime object of these annual meetings is dissemination of knowledge and the conduct of essential

business.

Following the trend of the times, the local Arrangements Committee was able to reduce convention expenses enough to lower the registration fee from \$5.00 to

\$3.50.

The Committee has discussed with the Editors of Cereal Chemistry ways and means of increasing the income of the Journal. Advertising is an important source of revenue. Members of the Association do not lend their support to the Managing Editor as they should. Cereal Chemists usually select their own purchases. How many chemists mention to the chemical supply house when placing an order that they saw their advertisement in Cereal Chemistry? This simple statement carries much weight.

A charter of a new section of the A. A. C. C. has been granted today. This section was organized in Texas and will be called, "The Lone Star Section." The officers are P. W. Preston, Chairman, F. E. Findley, Vice-Chairman, and Rolfe L.

Frye, Sec.-Treas. They have started auspiciously with 16 members.

The Executive Committee has been besieged with invitations for the 1934 convention. In accordance with recent custom, the members of the Association will have an opportunity later to indicate their preferences for the convention city for the guidance of the Executive Committee, whose responsibility it is to make the final selection.

The Chairman wishes to acknowledge the splendid cooperation of the members of the Committee and also of the Secretary-Treasurer during the past year.

V. E. Fisher moved that the report of the Executive Committee be accepted. Seconded, carried.

Report of the Membership Committee

W. A. Richards, Chairman

The Membership Committee, with the help of Mr. Mize and all Association members, carried on a continuous campaign for new members. We can report to date:

28 new, active members 1 corporation member 7 reinstated, active members

added to our membership since the 1932 convention.

C. E. Mangels moved that the report of the Membership Committee be accepted. Seconded, carried.

Report of the Employment Committee

C. B. Morison, Chairman

Letters, correspondence from May 23, 1932 to June 5, 1933	110
Letters from May 29, 1925 to May 23, 1932	080
Decisions Ciled	707
Positions filled	4
Employers requesting assistance	(
Names registered from May 23, 1932 to June 5, 1933	16
Previous names registered	190
Total names registered	206

J. A. Dunn moved that the report of the Employment Committee be accepted. Seconded, carried.

Report of the Publicity Committee

C. G. Harrel, Chairman

The Publicity Committee has performed the usual duties of this office, transmitting to the press and trade journals many news items concerning our Convention activities.

In addition to this, throughout the year we have sent to our membership news of sickness of various members of our organization.

Immediately following the election of our officers telegrams were dispatched to

the heads of their various organizations.

Another valuable activity of the Publicity Committee is the identification and information card which contains the lists of all of our Sections, together with their chairmen and the time and meeting place. In addition, this list contains the addresses of all of the past presidents,

We urge you to use this list and when present in these respective cities com-

municate with these units of our National organization.

Daily reports of our National Meeting in Chicago on June 5-8 have been mailed to all of the trade papers.

C. B. Morison moved that the report of the Publicity Committee be accepted. Seconded, carried.

Report of Committee on Osborne Medal Award

Paul Logue, Chairman

Your Committee on the Osborne Medal Award has no recommendation to make to the Association of a recipient for the medal at the present time. This is not from the lack of activity on the part of individuals in cereal chemistry, but because of adherence to the expressed wish of the Association that the medal not be awarded too often. In order that your Committee might not be idle during its tenure of office and might not return empty handed, it offers the names of several men who have been sufficiently active in cereal chemistry work to justify their consideration by subsequent committees as possible recipients of the medal. It is the feeling that if such action be taken by subsequent committees the information collected will focus the attention upon the most outstanding men in the field so that when the time comes for the selection of another medalist it may be felt that at the moment, at least, he is the most outstanding contributor to the science of cereal chemistry. These names will be made a part of the committee's records and passed on to the next committee.

Paul Logue moved that the report of Committee on Osborne Medal Award be accepted. Seconded, carried.

Report of the History Committee

·R. Wallace Mitchell, Chairman

The report of this Committee is primarily contained in the manuscript, "History of the Association" which is herewith placed in the hands of the officers.

It may not be out of order to make one or two comments relative to the progress that the committee has been able to achieve during the course of the past year. This committee has served on this project for several years and we are not particularly proud of the progress that has been made but we feel that at this time we have the record in a satisfactory shape for the period covered. The point that remains unsatisfactory to us is in acknowledging that the work has been completed only so far as the year 1928.

The committee has considerable material assembled covering the years 1929 to date, but it is our experience it is not possible to put into final form the record for any particular year until time itself has permitted the essentials of true progress to stand out from the routine activities that occupy the minds and time of the officers and members. It may be interesting to the members to know that the ideas and material contributed recently have necessitated an almost complete rewriting of the history as submitted last year. We acknowledge, at this time, the generous assistance which we have received from R. J. Clark in the work of the year.

We submit the manuscript of the History, at this time, in a form that will permit changes in assembling the data and the inclusion of new material which may come to future committees without making necessary the complete rewriting of the manuscript. We offer the suggestion that the Executive Committee be charged with reviewing this present manuscript and instructed to approve or correct it and then take suitable action to insure that the work be made official.

The committee wishes to thank all of those members who have so generously given of their time and thought to make possible the record as here presented. We would also take this occasion to recommend to the membership that they cooperate promptly and to the best of their ability with the committee that may be appointed to carry on the work which this committee has sought to accomplish.

R. W. Mitchell moved that the report of the History Committee be accepted. Seconded, carried.

Report of the Committee on Milling Chemistry at Julius Rosenwald Museum of Science and Industry

F. L. Dunlap, Chairman

During the past year, the Committee on Milling Chemistry appointed for the purpose of cooperating with the Julius Rosenwald Museum of Science and Industry, has not been called on, hence it has no specific report to give.

It is possible that when conditions which have their cause in our present business depression have been rectified, the Committee may be called on, in which case,

it is hoped that it may then serve some useful purpose.

J. A. Dunn moved that the report of the Committee on Milling Chemistry at Julius Rosenwald Museum of Science and Industry be accepted. Seconded, carried.

Report of the Committee on Resolutions

H. G. Walter, Chairman

Whereas, The American Association of Cereal Chemists has been privileged to hold another successful convention, and

Whereas, the success of this convention has been due largely to the faithful service rendered by the officers and committees of this association,

Therefore, be it resolved, that the thanks of this association be extended to its officers who have so faithfully served during the past year: President, L. D. Whiting; Vice-President, R. C. Sherwood; Secretary-Treasurer, M. D. Mize; and to the Program Committee, C. B. Morison, Chairman; the Local Arrangements Committee, L. E. Jackson, Chairman; Committee on Standardization of Laboratory Baking, W. F. Geddes, Chairman, and to all other committees so successfully contributing to the year's work.

Be it further resolved, that the appreciation of the association be extended to the Editorial Staff of CEREAL CHEMISTRY for its faithful work during the past

Be it further resolved, that we express our thanks to Dr. Herman S. Bundeson, Director of the Health Department, City of Chicago, for the welcome to Chicago.

Be it further resolved, that we express our thanks to L. J. Schumaker, Chairman of the Board of Directors of the American Institute of Baking, and to Dr. Gustav Egloff, Research Director, Universal Oil Products Company, Chicago, for their fine addresses.

Be it further resolved, that our appreciation be expressed to the following contributors of the golf trophies: Central Scientific Company, Durkee Famous Foods, Inc., Provident Chemical Works, E. H. Sargent & Company, Swift & Company, Victor Chemical Works, Wallace & Tiernan Company, Inc., Washburn Crosby Inc., Wesson Oil & Snowdrift Sales Company.

Be it further resolved, that our appreciation be expressed to the Bausch & Lomb Company for the use of the Baloptican throughout the convention period.

Be it also resolved, that our thanks be extended to the Medinah Athletic Club for its courtesies.

Whereas, misfortune has befallen our fellow member Dr. Albert Cliffe, Be it resolved, that this association extend to him its deep sympathy and wishes for speedy recovery.

Be it further resolved, that out of respect for our late fellow members, Alfred W. Meyer and Fred L. Ward, communications be sent their families further expressing the deep sympathies of the association.

H. G. Walter moved that the Report of the Committee on Resolutions be accepted. Seconded, carried.

A communication of greeting was received and read from C. J. Patterson.

Report of the Nominating Committee

L. R. Olsen, Chairman

Election of officers:

President-R. C. Sherwood Vice-President—Mary M. Brooke Secretary-Treasurer—M. D. Mize Editor-in-Chief Cereal Chemistry-D. A. Coleman Managing Editor Cereal Chemistry-C. C. Fifield

R. C. Sherwood moved that the secretary-treasurer be given \$100.00 as a partial

appreciation of the work done during the past year. Seconded, carried.

A number of invitations to hold our 1934 convention in Toronto and Dallas were received and read. R. L. Frye presented an invitation from the Lone Star Section to make Dallas our convention city for 1934. H. G. Liggitt invited the association to select Denver as a convention city at any future date desirable to our members. L. D. Whiting presented an invitation to meet in Louisville.

Report of the Committee on Methods of Testing Cake and Biscuit Flours and

Mary M. Brooke, Chairman. Sub-report—by L. H. Bailey, "Standard Cake Baking Method", read by C. C. Fifield.

Sub-report—by Charles A. Glabau, "Relation of the Hydrogen-ion Concentration to the Standard Cake Baking Test", and "The Standardization of the Egg Albumin."

Sub-report—by W. E. Stokes, "Relation of Baking Powder Content to the Shortening Increment."

Sub-report—by H. G. L. Walter, "Tests for Biscuit and Self-Rising Flours."

H. G. L. Walter moved that this report be accepted. Seconded, carried. Sub-report—by J. A. Dunn, "Testing Biscuit and Cracker Flours." Dunn moved that this report be accepted. Seconded, carried.

Sub-report—by G. L. Alexander, "The Results of Bleaching Michigan Soft Winter Cake Flours."

Sub-report-by R. A. Barackman, "Score Card."

Report of the Committee on Definition of Moisture Basis for Laboratory Reports, R. K. Durham, Chairman. R. K. Durham moved that this report be accepted. Seconded, carried.

Report of the Committee on Testing Rye Flour, L. H. Bailey, Chairman; read by J. T. Flohil. J. T. Flohil moved that this report be accepted. Seconded,

Report of the Committee on Testing Pie Flours, A. A. Schaal, Chairman; read by G. N. Bruce. G. N. Bruce moved that the report be accepted. Seconded, carried.

Report of the Committee on Definitions of Technical Terms, Washington Platt, Chairman. Washington Platt moved that the report be accepted. Seconded, carried.

Meeting adjourned at 12:00 noon.

Meeting called to order by President Sherwood at 2:00 p.m.

C. S. Miner was introduced as chairman for the afternoon session.

Paper—" Diastatic Activity in Doughs and Suspensions", by Quick Landis. Paper—" Use of the Glass Electrode for Direct Measurement of Hydrogen-ion Concentration in Fermenting Doughs", by Quick Landis,
Paper—"Standard Baking Test", by D. W. Kent-Jones, read by C. B.

Morison.

Paper—"Correlation between Commercial and Laboratory Milling Tests", by C. H. Bailey and M. C. Markley; read by C. H. Bailey.

Paper—"Relative Baking Qualities of Commercially and Experimentally Milled Flours", by M. C. Markley and C. H. Bailey; read by M. C. Markley.

Paper—"Studies on Test Weight and Flour Yielding Capacity of Wheat", by C. E. Mangels.

Paper—"Economical Muffle Furnace Operation", by C. G. Harrel and S.

Duoos; read by C. G. Harrel.

Paper—"An Improved Method for Determining Gasoline Color Value and its Relation to Carotin Content", by W. F. Geddes, D. S. Binnington and A. G. O. Whiteside; read by W. F. Geddes.

Paper—"The Measurement of Color in Flour and Bread by means of Maxwell

Discs", by J. C. Baker.

Report of the Committee on Methods of Analysis, C. E. Mangels, Chairman. Sub-report—by E. G. Bayfield, "Viscosity Test for Soft Winter Wheat

Sub-report—by F. A. Collatz, "Chemical Leavening Agents." Sub-report—by C. F. Davis, "Selenium as a Kjeldahl Catalyst."

Sub-report—by J. T. Flohil, "Volumetric Copper Reduction Method for Sugar Determination."

Meeting adjourned 6:00 p.m.

Sub-report—by A. E. Treloar, cooperatively with the Northwest Section, A. A. C. C., "An Evaluation of Systematic and Random Errors in Protein, Moisture, and Ash Determinations", read by R. C. Sherwood.

C. E. Mangels moved that the recommendation of the Committee on the Methods of Analysis be accepted. Seconded, carried.

Thursday, June 8

Joint session of the American Association of Cereal Chemists and the Association of Operativers Millers with the co-operation of the American Society of Bakery Engineers was called to order at 9:00 a.m., by L. D. Whiting.

Meeting placed in charge of C. O. Swanson, chairman for the morning. C. O. Swanson delivered an address of greeting to the Millers and Bakery Engineers calling attention to the object of a joint meeting.

C. M. Parks, President of the Association of Operative Millers, brought a message of greetings from the Operative Millers and gave a short talk on the importance of the production of quality flour.

L. D. Whiting, retiring President, delivered a message of welcome to the Operative Millers and Bakery Engineers calling attention to the importance of the

three associations in the production of quality products.

Paper—"Value of the Laboratory to the Operative Miller", by Paul K.
Fisher, Superintendent, Commercial Milling Company, Detroit, Mich.
Paper—"The Function of the Mill Laboratory", by R. C. Sherwood.
Paper—"What Information can the Mill Laboratory give the Baker on Bak-

ing Value of Flour", by H. D. Liggitt.

Paper-"What does the Baker Want to Know From a Flour Report?" by Carl Pickering, President, American Society of Bakery Engineers; read by Victor E. Marx.

Paper—" Testing Cake Flour", by G. L. Alexander.
Paper—" Testing Cracker Flour", by R. M. Bohn.
Paper—" Importance of Gassing Power", by R. K. Durham.

Prof. B. W. Dedrick, Instructor in Milling Engineering of Pennsylvania State College, was introduced and gave a few remarks on flour production and testing. Meeting adjourned at 12:00 noon.

Meeting called to order by retiring President L. D. Whiting at 1:30 p.m. C. B. Morison, chairman for the afternoon, was placed in charge of the

R. W. Mitchell moved that the sentiments of the following resolutions be placed in a permanent form and delivered to our retiring President, L. D. Whiting:

"To L. D. Whiting, our Retiring President, the members of this Society wish to express the sincere gratitude and individual appreciation of the executive leadership, the untiring efforts and unselfish sacrifices which have characterized your service to our Society during the past year. In this way we wish to express to you the thought that you have endeared yourself to the membership in a manner entirely outside of official relations. We have learned to admire you because of your many outstanding qualities-courtesy, friendliness, and patience-which have cemented a bond of esteem to make the memory of the past year richer for each one of us.

We cherish the hope that we may enjoy the privilege of your association for many years to come.' Seconded, carried.

Paper-" Cereal Foods and Their Advertising", by Raymond Hertwig, Secretary, Committee on Foods, American Medical Association.

Paper—"Fermentation Response and Fermentation Tolerance", by Quick Landis and Jacob Freilich; read by Jacob Freilich.

Paper—"The Shortening Value of Edible Fats", by Jennie D. Fisher.
Paper—"The Influence of Humidity and Carbon Dioxide upon the Development of Mold on Bread", by O. Skovholt and C. H. Bailey; read by O. Skovholt.
Paper—"Destroying Mold Spores on Bread by Ultra Violet Light Irradiation", by J. W. Read.
W. F. Geddes, Chairman of the Committee on Standardization of Laboratory

Baking, moved that mechanical mixing by the Hobart-Swanson Mixer be made the official method of mixing for the A. A. C. C. baking tests. Seconded, carried. Paper—"Non-Survival of Red Mold of the Monilia Sitophila Group at Baking Temperature", by C. B. Morison.

ing Temperature", by C. B. Morison.

Paper—"Practical Observations on Bread and Cracker Flours", by J. Micka.

Paper—"Some Experiences with Wheat Meal Fermentation Time.—Test for

Evaluating Wheats" by O. B. Winter.

Paper—"European Development of Farinograph and Methods from the Viewpoint of Practice", by C. W. Brabender.

Convention adjourned at 5:00 p.m. by President Sherwood.

REGISTRATION OF CONVENTION, CHICAGO, ILLINOIS **JUNE 5-JUNE 8, 1933**

Members

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H. D. Liggitt, Jr.
Paul Logue Faul Logue
L. H. Luedemann
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R. M. McKinstrie
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Josh Manischewitz Max C. Markley Victor E. Marx H. S. Mitchell
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August J. Pacini August J. Pacini M. H. Parlin Paul Pelshenke Washington R. B. Potts Hamilton W Washington Platt Hamilton W. Putnam Glenn L. Pyle W. L. Rainey

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V. Shiple
Wm. Siedhoff
E. Singruen
Oscar Skovholt

Edw. E. Smith
W. E. Stokes
Betty Sullivan
C. O. Swanson
John E. Tatar
W. Kedzie Teller
E. F. Tibbling
H. O. Triebold
Edgar L. Ulrey
C. G. Vaupel
Edwin A. Vaupel
H. F. Vaupel

James D. Veron
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H. E. Weaver
S. O. Werner
Hannah L. Wessling
J. W. Whitacre
Lawrence D. Whiting
A. K. Whittaker
A. Wiesehahn
O. B. Winter
W. B. Young
J. E. Zvanovec

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Mrs. C. H. Bailey
Mrs. W. J. Balmer
Mrs. H. J. Brownlee
Mrs. G. S. Bratton
Mrs. C. L. Brooke
Mrs. D. A. Coleman
Mrs. A. E. Curtis
Mrs. C. F. Davis
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Mrs. L. E. Jackson
Mrs. J. C. Lankenau
Mrs. L. E. Leatherock
Miss Esther Leatherock
Miss Ruth Leatherock
Mrs. H. D. Liggitt
Mrs. Paul Logue
Mrs. L. H. Luedemann

Mrs. J. M. Lugenbeel and daughter
Mrs. F. J. Lumsden
Mrs. C. H. Mac Intosh
Mrs. P. E. Minton
Mrs. M. D. Mize
Mrs. G. Moen
Mrs. R. B. Potts
Mrs. Glen L. Pyle
Mrs. W. A. Richards
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Mrs. H. E. Weaver
Mrs. L. D. Whiting
Miss Anna Margaret
Whiting
Mr. Larry Whiting

Miss Jennie B. Nashold
Mrs. O. B. Winter
H. E. Barnard
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John W. Eckhart
Gustav Egloff
Theo B. Hansen
Roy W. Hanson
J. P. Henderson
Stanley M. Jackson
Geo. F. Long
Harry J. Loving
F. N. Peters, Jr.
A. W. Putland
L. J. Schumaker
J. T. Sullivan
Geo. W. Thoms
Earl Tuter
Otto Walther

NEW PUBLICATIONS

Report of the First International Bread Congress at Rome, June 21 to 24, 1932. 18 × 25 cm. paper. 517 pp. Published by Federazione Nazionale del Panificatori ed Affini, Piazza Sidney Sonnino, 2., Rome, Italy. Price 40 lire (about \$3.00 present rate of exchange).

This volume should be of considerable interest not only to cereal chemists, but to those likewise interested in the economics of bread production. The volume is a complete record of the various papers read at the First International Bread Congress which was held at Rome and Bologna, Italy, in June, 1932.

A wide range in subject matter is covered including discussions with respect to the economic and social status of bread production, numerous papers relative to chemistry of bread production, methods of analysis and interpretation.

The papers as printed are in the native tongue of the author. It is to be regretted that no contributions were made to the Congress by those interested in the production of bread in the United States.

Milling and Baking Quality of Wheat Cultivated in Poland, Crop Year 1931.

Bulletin 9. Bureau of Cereal Crops, Department of Agriculture, Warsaw, Poland. 89 pp. + 5 pp. illus.

This volume, which is printed in Polish, is devoted to a discussion of the milling and baking properties of the important wheat varieties grown in the crop year 1931.

Kotimaisen Viljan Laatua Koskevia Tutkimuksia VI. Valtion Maatalouskoetoiminnan Julkaisuja No. 52. (Über Die Backfähigheit Einiger in Finnland Angebauten Winter und Sommerweizensorten 1928–1929.) 16 × 24 cm. 145 pp. + 12 pp. illus. By E. S. Tomula. Helsinki, 1933.

This is a comprehensive study made of the baking quality of the more important varieties of wheat of both spring and winter habit grown in Finland. Most of the text is in Finnish, but there is also a very comprehensive and well written summary given in German.